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[1940] *The Constituents of Natural Phenolic Resins. Part XVIII.* 1321

**250.** *The Constituents of Natural Phenolic Resins. Part XVIII. 1:2:3:4-Tetrahydronaphthalene-2:3-dicarboxylic Acid and the 1-Phenyl Derivative.*

By Robert D. Haworth and Frank H. Slinger.

1:2:3:4-Tetrahydronaphthalene-2:3-dicarboxylic acid, best prepared by the reduction of naphthalene-2:3-dicarboxylic acid, has been obtained in cis- and trans-forms, and the constitutions have been determined by the resolution of the *trans*-acid. Boiling acetic anhydride converts the trans- into the cis-*anhydride*, and sodium ethoxide transforms the cis- into the trans-*methyl* ester. The cis- and the trans-*form* of the lactone (II) have also been prepared.
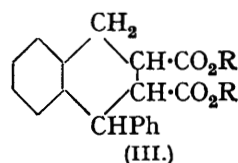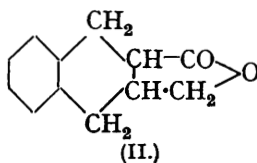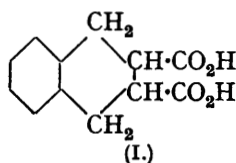
1-Phenyl-1:2:3:4-tetrahydronaphthalene-2:3-dicarboxylic acid (III; R = H) has been separated into a number of stereoisomeric forms. Three acids and anhydrides, and four dimethyl esters have been isolated in a pure condition, and an examination of the stabilities of the anhydrides and esters towards acetic anhydride and sodium ethoxide respectively, combined with an assumption based upon the instability of *cis*-cinnamic acid, has been used in the allocation of configurations to the stereoisomeric modifications. The three anhydrides have been converted into three isomeric benzo-tetrahydrofluorenonecarboxylic acids (IV; R = $CO_2H$), which in accordance with the suggested configurations yield two benzotetrahydrofluorenones (IV; R = H) on decarboxylation.

During this series of investigations numerous problems have arisen concerning the stereo-chemical configuration of trisubstituted tetrahydronaphthalene derivatives. For instance, in Part XVI (J., 1939, 1237) it was observed that reduction of a number of 1-phenyl-naphthalene-2:3-dicarboxylic acids yielded a mixture of stereoisomeric modifications of the corresponding tetralin derivatives, and evidence was obtained of frequent optical inversions during subsequent reactions with these compounds. In order to throw light on these and similar problems, information concerning the relative stability of less complex but related molecular structures was desirable, and an examination was first made of the cis- and the *trans*-form of 1:2:3:4-tetrahydronaphthalene-2:3-dicarboxylic acid (I).

In the course of their classical experiments on cyclic compounds, Perkin and Baeyer (*Ber.*, 1884, **17**, 1448; J., 1888, **53**, 12) prepared one form of the acid (I) from o-xylylene dibromide and ethyl ethanetetracarboxylate. This work has been confirmed; an acid, m. p. 196°, was obtained in small yields, which gave an anhydride, m. p. 185°, on pyrolysis. No indications of the production of a stereoisomeric modification were obtained and attempts to resolve the acid were unsuccessful, but the paucity of our material precluded extensive investigation and reliable conclusions.

A supply of naphthalene-2:3-dicarboxylic anhydride, which was kindly placed at our disposal by Dr. Wilson Baker, provided a new and more convenient route to the tetrahydro-acid (I). Reduction of naphthalene-2:3-dicarboxylic acid with sodium amalgam in hot alkaline solution yielded a mixture, m. p. 185—190°, of stereoisomeric forms of the tetra-hydro-acid (I), which could not be separated by fractional crystallisation. When this mixture was refluxed with acetyl chloride, an *anhydride*, m. p. 225—226°, separated from the hot solvent, and a stereoisomeric anhydride, m. p. 183°, identical with the anhydride prepared by Perkin and Baeyer (*loc. cit.*), was recovered from the solution. The tetrahydro-acid (I) obtained by hydrolysis of the lower-melting anhydride melted at 195° and was identical with the acid obtained by Perkin and Baeyer, and our failure to resolve the larger quantities of acid, obtainable by the new method, indicated that the acid, m. p. 105°, was the *cis*-modification. This conclusion was established by hydrolysis of the anhydride, m. p. 225—226°, to the *trans*-acid (I), m. p. 226—227°, which was readily resolved by means of strychnine. The acid *strychnine* salts were separated by fractional crystallisation, and decomposition yielded the d- and the l-*form* of the *trans*-acid (I), m. p. 182—183°, with $[\alpha]_D$ + 85·5° and − 85·0° respectively in chloroform solution. The configurations of the two forms of the acid (I) have also been confirmed by measurements of the dissociation constants, which were made by Dr. J. C. Speakman and will be fully reported later.

Experiments on the relative stabilities of the stereoisomerides were then undertaken. The *trans*-anhydride, m. p. 225—226°, was completely converted into the *cis*-form, m. p.

$$
\begin{array}{ccc}
\text{CH}_2 & \text{CH}_2 & \text{CH}_2 \\
\text{CH·CO}_2\text{H} & \text{CH—CO} & \text{CH·CO}_2\text{R} \\
\text{CH·CO}_2\text{H} & \text{CH·CH}_2 \!\!>\!\! \text{O} & \text{CH·CO}_2\text{R} \\
\text{CH}_2 & \text{CH}_2 & \text{CHPh} \\
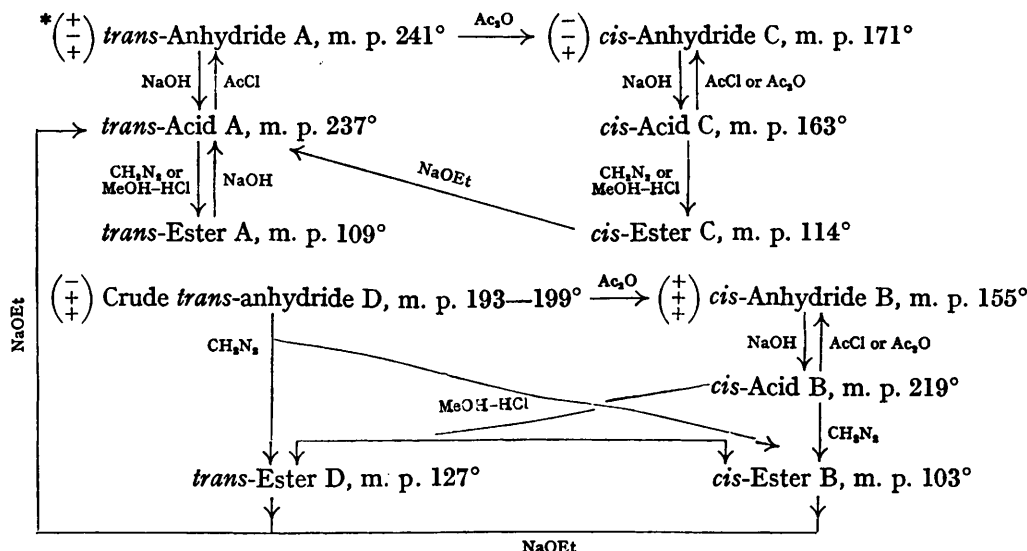\text{(I.)} & \text{(II.)} & \text{(III.)}
\end{array}
$$

185°, by boiling with acetic anhydride for 15 minutes, and the *cis*-anhydride was obtained exclusively by dehydrating the mixture of tetrahydro-acids (I), m. p. 185—190°, with acetic anhydride. Esterification of the *cis*- and the *trans*-acid, either by means of the Fischer–Speier or the silver salt method, yielded the corresponding *methyl* esters, m. p. 68° and 45° respectively, and it has been shown that the *cis*-ester is converted into the *trans*-modification by the action of sodium ethoxide. The relative stabilities of the anhydrides and esters are consistent with stereochemical theory and are in agreement with similar observations in the hexahydrophthalic acid series (Baeyer, *Annalen*, 1890, **257**, 213; Hückel and Goth, *Ber.*, 1925, **58**, 447).

Reduction of the *cis*- and the *trans*-anhydride with aluminium amalgam yielded the corresponding *lactones* (II), m. p. 133—134° and 156° respectively. Alkaline hydrolysis of these lactones yielded solutions of the corresponding hydroxy-acids, from which the original lactones were recovered upon acidification. These observations contrast markedly with previous experience with *d-iso*matairesinol dimethyl ether (J., 1938, 797), which undergoes rapid optical inversion under similar alkaline conditions.

The experiments were then extended to the case of 1-phenyl-1 : 2 : 3 : 4-tetrahydro-naphthalene-2 : 3-dicarboxylic acid (III; R = H). This acid, readily obtained by reduction of 1-phenylnaphthalene-2 : 3-dicarboxylic acid with sodium amalgam (Michael and Bucher, *Amer. Chem. J.*, 1898, **20**, 89; Stobbe, *Ber.*, 1907, **40**, 3372), may exist in four racemic modifications. It was recently shown (J., 1939, 1239) that the crude reduction product, m. p. 170—180°, yielded on crystallisation an acid (III; R = H), m. p. 209° (now raised to 218°; p. 1325), identical with that described by earlier workers, and evidence of isomeric forms was obtained. These have now been subjected to a more extensive investigation. The crude acid, m. p. 170—180°, was converted by acetyl chloride into a mixture of anhydrides, from which *anhydride A*, m. p. 241°, *anhydride B*, m. p. 155°, and in smaller quantity *anhydride C*, m. p. 171°, were isolated by fractional crystallisation. Cautious hydrolysis gave the corresponding *acids*, A, m. p. 237°, B, m. p. 219°, identical with the purified acid obtained from the crude reduction product (III; R = H), and C, m. p. 163°. Each acid reverted to its anhydride on treatment with acetyl chloride, and on treatment with diazomethane in methyl-alcoholic solution the acid or anhydride yielded the corresponding *dimethyl* ester (III; R = Me), A, m. p. 109°, B, m. p. 103°, and C, m. p. 114°.

The stability of the acids and esters towards acetic anhydride and sodium ethoxide was examined. Anhydrides B and C were unaffected by acetic anhydride, but on boiling anhydride A was completely transformed into anhydride C, and it was concluded that anhydride A was one of the two possible *trans*(2 : 3)-anhydrides and B and C represented the two *cis*(2 : 3)-modifications. Under the influence of either sodium ethoxide or hydroxide the three methyl esters A, B, and C were converted into the *trans*(2 : 3)-acid A, and analogy with observations on acid (I) confirm the *cis*(2 : 3)-structure for acids B and C. The optical inversion of the *cis*(2 : 3)-methyl ester to acid A was unexpected; the production of the fourth modification of acid (III; R = H) was expected. Evidence of the fourth form, *viz.*, *trans*(2 : 3)-acid D, was obtained from two sources. First, the anhydride mother-liquors, from which anhydrides A, B, and C were separated, yielded a crude specimen, m. p. 193—199°, of *trans*(2 : 3)-anhydride D, which on methylation with diazomethane in methyl-alcoholic solution gave a mixture of the *cis*(2 : 3)-methyl ester B, and a new *methyl* ester, m. p. 126—127°, which is regarded as the *trans*(2 : 3)-ester D. Secondly, the same dimethyl ester D was also obtained as a result of an examination of the Fischer–Speier esterification of the stereoisomeric anhydrides of the acid (III; R = H); the *trans*(2 : 3),

A, and *cis*(2 : 3), C, anhydrides gave the corresponding dimethyl esters, but the *cis*(2 : 3)-anhydride B yielded a mixture of the corresponding ester B and the *trans*(2 : 3)-ester D, m. p. 127°. Attempts to hydrolyse the *trans*(2 : 3)-ester D to the corresponding acid resulted in the production of the *trans*(2 : 3)-acid A, and the instability of the *trans*(2 : 3)-acid D is further illustrated by the observations that the crude anhydride D, m. p. 193—198°, was completely converted into the *cis*(2 : 3)-anhydride B by the action of acetic anhydride, and into the *cis*(2 : 3)-acid B by mild hydrolysis. The changes described above are summarised below.

$*\begin{pmatrix}+\\-\\+\end{pmatrix}$ *trans*-Anhydride A, m. p. 241° $\xrightarrow{Ac_2O}$ $\begin{pmatrix}-\\-\\+\end{pmatrix}$ *cis*-Anhydride C, m. p. 171°

NaOH ↓↑ AcCl          NaOH ↓↑ AcCl or Ac₂O

→ *trans*-Acid A, m. p. 237°          *cis*-Acid C, m. p. 163°

CH₂N₂ or MeOH–HCl ↓↑ NaOH     $\xleftarrow{NaOEt}$     CH₂N₂ or MeOH–HCl ↓

*trans*-Ester A, m. p. 109°          *cis*-Ester C, m. p. 114°

$\begin{pmatrix}-\\+\\+\end{pmatrix}$ Crude *trans*-anhydride D, m. p. 193—199° $\xrightarrow{Ac_2O}$ $\begin{pmatrix}+\\+\\+\end{pmatrix}$ *cis*-Anhydride B, m. p. 155°

CH₂N₂          NaOH ↓↑ AcCl or Ac₂O

*cis*-Acid B, m. p. 219°

MeOH–HCl          ↓ CH₂N₂

*trans*-Ester D, m. p. 127°          *cis*-Ester B, m. p. 103°

NaOEt

\* These configurations are based on considerations discussed below. The bottom and the top sign refer to the configurations of carbon atoms 1 and 3 respectively.

The relative stabilities of the anhydrides and the esters towards acetic anhydride and sodium ethoxide respectively enable the configurations of carbon atoms 2 and 3 to be determined with some certainty, but the configuration of carbon atom 1 presents a more difficult problem. The instability of the *trans*(2 : 3)-ester D and its conversion into *trans*(2 : 3)-acid A has an important bearing on this problem. If the inversion of esters (III; R = Me) in the presence of sodium ethoxide involves the intermediate formation of an enolic modification, the positions taken up by the hydrions on subsequent ketonisation will be determined by two repulsive factors. First, the mutual repulsion of the two carbomethoxy-groups will facilitate inversion of a *cis*(2 : 3)- into a *trans*(2 : 3)-arrangement, and secondly the repulsion between phenyl and carbomethoxy-groups, illustrated by the greater stability and smaller dissociation constant of *trans*- compared with *cis*-cinnamic acid, will favour inversion of a *cis*(1 : 2)- into a *trans*(1 : 2)-configuration. Consequently the stable *trans*(2 : 3)-acid A may be given the *trans*(1 : 2)*trans*(2 : 3)-configuration, the *cis*(1 : 2)*trans*(2 : 3)-structure is assigned to the unstable acid D, and the *cis*-acids B and C are regarded as *cis*(1 : 2)*cis*(2 : 3) and *trans*(1 : 2)*cis*(2 : 3) respectively. The interconversions of the A–C and B–D pairs involve inversion at the exposed asymmetric centre, and the inversion at the sterically hindered carbon atom 2, when esters B and D are converted into acid A, is ascribed to the repulsion between the phenyl and carbomethoxy-groups. As some *trans*-ester D is obtained by Fischer–Speier esterification of *cis*-anhydride B, the absence of *trans*-ester A during similar esterification of *cis*-anhydride is surprising, but we do not regard this as a serious objection to the suggested configurations.

1-Phenylnaphthalene-2 : 3-dicarboxylic anhydride is converted by either concentrated sulphuric acid (Stobbe, *loc. cit.*, p. 3383) or aluminium chloride (Schaarschmidt, *Ber.*, 1915, **48**, 1826) into the red 3 : 4-benzofluorenone-1-carboxylic acid. The anhydrides A, B, and C of acid (III; R = H) were all sulphonated by cold concentrated sulphuric acid, but with

aluminium chloride in nitrobenzene solution they were converted into three colourless stereoisomeric 3 : 4-*benzo*-1 : 2 : 10 : 11-*tetrahydrofluorenone*-1-*carboxylic acids* (IV; R =

(IV.)

CH$_2$  CHR  CH  CH  CO

(V.)

CH$_2$  CH  CHR  CH  CO
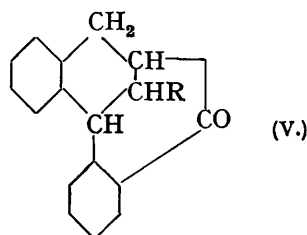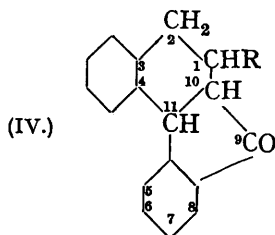
CO$_2$H), *A* [*trans*(10 : 11)*trans*(1 : 10)], m. p. 204°, *B* [*cis*(10 : 11)*cis*(1 : 10)], m. p. 220°, and *C* [*trans*(10 : 11)*cis*(1 : 10)], m. p. 164°. On dehydrogenation with selenium all three acids yielded 3 : 4-benzofluorenone, m. p. 164°, and consequently the alternative tetralone structure (V; R = CO$_2$H) may be excluded for the monocarboxylic acids A, B, and C. Decarboxylation of the acids (IV; R = CO$_2$H) was effected by boiling with quinoline in the presence of copper powder. The two *trans*(10 : 11)-monocarboxylic acids A and C yielded the same trans(10 : 11)-3 : 4-*benzo*-1 : 2 : 10 : 11-*tetrahydrofluorenone* (IV; R = H), m. p. 163°, and the *cis*(10 : 11)-monocarboxylic acid B gave the isomeric *cis*(10 : 11)-modification, m. p. 134°, of the ketone (IV; R = H). These decarboxylation experiments were made on a very small scale, and the results, indicating a surprising stability of the *cis*- and *trans*-forms of the ketone (IV; R = H), require confirmation, which will be sought when opportunities arise for a continuation of this work.

The *trans*(2 : 3)-configuration has been established for several naturally occurring lignans, and the observed stability of the *trans*(1 : 2)*trans*(2 : 3)-acid (III; R = H) indicates that the 1-phenylnaphthalene representatives of the lignan family, including conidendrin, *iso*olivil, and podophyllotoxin, possess this stable *trans*(1 : 2)*trans*(2 : 3)-structure.

## EXPERIMENTAL.

*Reduction of Naphthalene-2 : 3-dicarboxylic Acid.*—Naphthalene-2 : 3-dicarboxylic anhydride (2 g.), m. p. 254°, was dissolved in 10% methyl-alcoholic sodium hydroxide (10 c.c.), diluted with hot water (200 c.c.), and 4% sodium amalgam (400 g.) added. After being stirred for 12 hours on the water-bath in a stream of carbon dioxide, the solution was filtered and concentrated under reduced pressure to approximately half bulk, and the product liberated by acidification was collected and washed with cold water. After crystallisation from hot water the mixture of the *cis*- and the *trans*-form of the acid (I) was obtained in prisms (2 g.), m. p. 185—190° (Found : equiv., 109. C$_{12}$H$_{12}$O$_4$ requires equiv., 110).

*Separation of the* cis- *and the* trans-*Form of* (I).—The mixture (5 g.) described above was refluxed with freshly distilled acetyl chloride (50 c.c.). The acids rapidly dissolved and the trans-*anhydride*, which gradually separated from the hot solution, was collected after 3 hours and recrystallised from acetyl chloride, forming hexagonal prisms (1·3 g.), m. p. 225—226° (Found : C, 70·9; H, 5·0. C$_{12}$H$_{10}$O$_3$ requires C, 71·3; H, 4·9%). The acetyl chloride filtrate was evaporated to dryness, and the residue crystallised from benzene, yielding the cis-*anhydride* in rectangular prisms (2·95 g.), m. p. 183° (Found : C, 71·3; H, 5·3%). This *cis*-anhydride was later obtained in a form which crystallised in hexagonal prisms, and either form could be obtained by inoculating a benzene solution of the anhydride with the appropriate crystal.

Hydrolysis of the anhydrides was effected by suspending the finely powdered anhydride in a little boiling water and gradually adding 10% sodium hydroxide solution until a faint, permanent, alkaline reaction to phenolphthalein was obtained; acidification of the cooled solution precipitated the acid. The cis-*acid* (I) separated from 20% methyl alcohol in large prisms, m. p. 194—195° (Found : C, 65·2; H, 5·3. C$_{12}$H$_{12}$O$_4$ requires C, 65·5; H, 5·5%), and gave an acid strychnine salt separating from methyl alcohol–chloroform in rhombic plates, which in chloroform solution (*c*, 1·00) gave $[\alpha]_D^{17°}$ — 45°, unchanged by further crystallisation. The *methyl* ester of the *cis*-acid, prepared either by refluxing the acid with 3% methyl-alcoholic hydrogen chloride (5 parts) for 4·5 hours, or by boiling an ethereal suspension of the dried silver salt, precipitated by the addition of silver nitrate to a neutral solution of the ammonium salt, with excess of methyl iodide for 24 hours, separated from ligroin in slender prisms, m. p. 68—

68·5° (Found : C, 67·3; H, 6·4. $C_{14}H_{16}O_4$ requires C, 67·6; H, 6·5%), which yielded the *cis*-acid on hydrolysis with hot aqueous sodium hydroxide.    The trans-*acid* (I) separated from 50% alcohol in large prismatic plates, m. p. 226—227° (Found : C, 65·0; H, 5·7%), and the *methyl* ester, prepared by either method described above in the case of the *cis*-ester, crystallised from ligroin in hexagonal prisms, m. p. 44·5—45° (Found : C, 67·8; H, 6·5%).    The methyl ester of the *cis*-acid (0·5 g.) was refluxed for 3 hours with a solution of sodium (0·05 g.) in absolute alcohol (10 c.c.).    The alcohol was removed, water added, and the product, isolated with ether, identified as the methyl ester of the *trans*-acid.

*Resolution of the* trans-*Form of Acid* (I).—The *trans*-acid (0·75 g.), m. p. 226—227°, and strychnine (1·4 g.) were mixed in chloroform (20 c.c.), and the solution diluted with alcohol (70 c.c.) and concentrated until crystallisation commenced.    The *strychnine* salt of the *l*-acid was collected and crystallised from alcohol–chloroform ; slender needles (0·9 g.), m. p. 170—180° (Found : C, 69·3; H, 6·3. $C_{12}H_{12}O_4,C_{21}H_{22}O_2N_2,H_2O$ requires C, 69·2; H, 6·3%), were obtained, which were too sparingly soluble in cold solvents for the determination of $\alpha_D$ value. The combined mother-liquors gave on concentration first a small amount of unchanged strychnine and then the *strychnine* salt of the *d*-acid, which separated from alcohol in stout prisms (1·15 g.), m. p. 195—240° (Found : C, 71·2; H, 6·9.  $C_{12}H_{12}O_4,C_{21}H_{22}O_2N_2$ requires C, 71·4; H, 6·1%). In alcohol (*c*, 2·00) it gave $[\alpha]_D^{16°} + 36\cdot5°$.

The strychnine salts, suspended or dissolved in chloroform, were decomposed by shaking with aqueous ammonia, and the acids liberated by acidification of the alkaline liquors.    The d- and the l-*acid* separated from acetone–benzene in slender prisms, m. p. 182—183° (Found for the *d*-acid : C, 65·5; H, 5·0.   Found for the *l*-acid : C, 65·5; H, 5·5.  $C_{12}H_{12}O_4$ requires C, 65·5; H, 5·5%).    An equimolecular mixture of the two melted at 215—220°.   In chloroform solution (*c*, 1·00) they had $[\alpha]_D^{16°} + 85\cdot5°$ and $- 85\cdot0°$ respectively.

cis- *and* trans-*Forms of the Lactone* (II) *of* 2-Hydroxymethyl-1 : 2 : 3 : 4-tetrahydronaphthalene-3-carboxylic *Acid*.—Difficulty was experienced in the discovery of suitable solvents for the reduction of the anhydrides of the acid (I).    Eventually a mixture of dioxan (20 parts), benzene (10 parts), and ether (10 parts) was employed in the case of the *cis*-anhydride, and dioxan (70 parts) was used for the *trans*-anhydride.    Water was gradually added during 48 hours to a mixture of the anhydride (0·5 g.) in a suitable solvent and aluminium amalgam (2·5 g.).    The alumina sludge, containing most of the product, was removed and decomposed with dilute sulphuric acid and the residue taken up in chloroform.    Configurational changes were not induced by this acid decomposition of the sludge, as identical products were obtained in slightly inferior yields by direct extraction of the alumina with chloroform or acetone.    The solvent was removed from the extract, and the residual oil crystallised from methyl alcohol.    The cis-*lactone* (II) separated in slender prisms (0·2 g.), m. p. 133—134° (Found : C, 76·6; H, 6·3.  $C_{12}H_{12}O_2$ requires C, 76·5; H, 6·4%), and the trans-*lactone* (II) in slender prisms (0·15 g.), m. p. 156° (Found : C, 76·3; H, 5·9%).    The *cis*- or the *trans*-lactone was refluxed with 10% methyl-alcoholic potassium hydroxide (10 parts) for 15 minutes, water added, the alcohol removed, and the solution of the hydroxy-acid salt acidified and boiled for 5 minutes ; the original lactones were recovered and no configurational alterations were observed.

*Anhydrides of* 1-Phenyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2 : 3-dicarboxylic *Acid* (III ; R = H).—The crude acid, m. p. 170—180°, prepared as described previously (J., 1939, 1239), yielded a homogeneous acid, m. p. 218—219° (decomp.) (Found : C, 73·1; H, 5·5.  Calc. for $C_{18}H_{16}O_4$ : C, 73·0; H, 5·4%), after repeated crystallisation from acetone–benzene.

The crude acid (4 g.), m. p. 170—180°, and freshly distilled acetyl chloride (50 c.c.) were allowed to react at room temperature for 24 hours.    The insoluble material (0·8 g.) was collected and crystallised from hot acetyl chloride ; trans(1 : 2)trans(2 : 3)-*anhydride A* was obtained in slender prisms, m. p. 240—241° (rapid heating) (Found : C, 77·2; H, 5·1.  $C_{18}H_{14}O_3$ requires C, 77·7; H, 5·0%).    The acetyl chloride was completely removed from the main filtrate, and the residue crystallised from a small amount of ether–light petroleum (b. p. 40—60°), which removed traces of oily impurities.    The solid product was then subjected to systematic fractional crystallisation from ether–light petroleum (b. p. 40—60°) ; the cis(1 : 2)cis(2 : 3)-*anhydride B* (2 g.), colourless rhombs, m. p. 155—156° (from light petroleum, b. p. 60—80°), or hexagonal plates, m. p. 155—156° (from benzene) (Found : C, 77·9; H, 5·0%), the trans(1 : 2)cis(2 : 3)-*anhydride C* (0·05 g.), slender prisms, m. p. 171—172° (from benzene) (Found : C, 77·5; H, 4·9%), and crude cis(1 : 2)trans(2 : 3)-*anhydride D*, m. p. 193—199° (Found : C, 77·6; H, 5·1%), were isolated.

The anhydrides were boiled for 3 hours with acetic anhydride (10 vols.), and the solvent removed under reduced pressure.   Under these conditions *cis*(1 : 2)*cis*(2 : 3)-anhydride B and

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*trans*(1 : 2)*cis*(2 : 3)-anhydride C were recovered unchanged, *trans*(1 : 2)*trans*(2 : 3)-anhydride A was converted into the *trans*(1 : 2)*cis*(2 : 3)-form C, and the crude *cis*(1 : 2)*trans*(2 : 3)-anhydride D was transformed into the *cis*(1 : 2)*cis*(2 : 3)-form B.

*The Dicarboxylic Acids* (III; R = H).—These were obtained by adding sodium hydroxide solution gradually to a boiling aqueous suspension of the corresponding anhydride until the solution was faintly alkaline to phenolphthalein. The solution was cooled and acidified, and the acid collected and dried. The trans(1 : 2)trans(2 : 3)-*acid A* separated from aqueous alcohol in small prisms, m. p. 236—237° (Found : C, 73·3; H, 5·5. $C_{18}H_{16}O_4$ requires C, 73·0; H, 5·4%). The cis(1 : 2)cis(2 : 3)-*acid B* crystallised from acetone–benzene in small prisms, m. p. 218—219° (Found : C, 72·9; H, 5·4%), identical with the acid obtained by repeated crystallisation of the crude acid, m. p. 170—180°, prepared by reduction of 1-phenylnaphthalene-2 : 3-dicarboxylic acid. The trans(1 : 2)cis(2 : 3)-*acid C* was obtained in prismatic plates, m. p. 162—163° from ether–light petroleum (b. p. 40—60°) (Found : C, 73·3; H, 5·7%).

*The Dimethyl Esters* (III; R = Me).—(a) *Esterification with diazomethane.* The acid (III; R = H) (0·1 g.) in methyl alcohol (2 c.c.) was treated with diazomethane (0·07 g.) in ether (30 c.c.). After 3 hours the solution was washed with sodium bicarbonate solution and dried, the solvent removed, and the esters, obtained in quantitative yields, crystallised from ether–light petroleum (b. p. 60—80°). The trans(1 : 2)trans(2 : 3)-*ester A*, slender prisms, m. p. 108—109° (Found : C, 73·9; H, 6·2. $C_{20}H_{20}O_4$ requires C, 74·0; H, 6·2%), cis(1 : 2)cis(2 : 3)-*ester B*, flat monoclinic prisms, m. p. 102—103° (Found : C, 74·2; H, 6·4%), and trans(1 : 2)cis(2 : 3)-*ester C*, slender prisms, m. p. 113—114° (Found : C, 73·9; H, 5·8%), were isolated from the corresponding acids. Esterification of the crude *cis*(1 : 2)*trans*(2 : 3)-anhydride D yielded a mixture of the *cis*(1 : 2)*cis*(2 : 3)-ester B (80% yield) and a smaller amount (20% yield) of the cis(1 : 2)trans(2 : 3)-*ester D*, which crystallised from light petroleum (b. p. 60—80°) in slender prisms, m. p. 126—127° (Found : C, 74·0; H, 6·2%), depressed by admixture with the esters A, B, and C.

(b) *Fischer–Speier esterification.* The acid (III; R = H) was refluxed for 3 hours with 3% methyl-alcoholic hydrogen chloride (5 c.c.). The alcohol was removed, the ester taken up in ether, washed with sodium bicarbonate solution, and dried, and the solvent removed. Acids A and C gave the corresponding dimethyl esters in yields exceeding 90%. Acid B (0·5 g.) gave a mixture, m. p. 80—90°, which was separated, roughly by hand picking and then completely by crystallisation of the fractions from ether–ligroin, into esters B (0·37 g.), m. p. 102—103°, and D (0·09 g.), m. p. 127—128°.

(c) *Hydrolysis of ester* (III; R = Me). The ester (0·2 g.) was refluxed for 3 hours with a solution of sodium (0·1 g.) in alcohol (5 c.c.). The alcohol was removed, water added, and the acid liberated by acidification and isolated with ether. In all cases the trans(1 : 2)trans(2 : 3)-acid A (0·13—0·18 g.), m. p. 236—237°, was isolated. 2N-Sodium hydroxide was used for the hydrolysis of the esters (III; R = Me) with the same result.

*3 : 4-Benzo-1 : 2 : 10 : 11-tetrahydrofluorenone-1-carboxylic Acid* (IV; R = $CO_2H$).—The anhydride (0·5 g.) and powdered aluminium chloride (0·4 g.) were dissolved in nitrobenzene (5 c.c.), and the solution heated at 100° for 3 hours. The nitrobenzene was removed in steam, and the residual aqueous liquor decanted from the semi-solid brown product, which was dissolved in warm dilute sodium hydroxide solution. The filtered alkaline solution was acidified, and the acid extracted with ether and dried over sodium sulphate. Most of the ether was removed, and ligroin gradually added; on standing, red crystals separated, and after several crystallisations from ether–ligroin or chloroform–ligroin, pure colourless specimens were obtained. The trans(10 : 11)trans(1 : 10)-*form A* of (IV; R = $CO_2H$) was obtained from chloroform–ligroin in prismatic plates (0·02 g.), m. p. 203—204° (Found : C, 77·7; H, 5·3. $C_{18}H_{14}O_3$ requires C, 77·7; H, 5·1%), the cis(10 : 11)cis(1 : 10)-*form B* separated from ether–ligroin in colourless prisms (0·23 g.), m. p. 220—221° (Found : C, 77·6; H, 5·2%), and the trans(10 : 11)cis(1 : 10)-*modification C* crystallised from ether–ligroin in clusters of needles (0·07 g.), m. p. 163—164° (Found : equiv., 277. $C_{18}H_{14}O_3$ requires equiv., 278).

The three monocarboxylic acids (IV; R = $CO_2H$) (0·1 g.) were heated with selenium (0·2 g.) at 280° for 24 hours. The product, isolated with chloroform and washed with dilute sodium hydroxide solution, was distilled at 0·1 mm. and purified by crystallisation from acetic acid; orange crystals, m. p. 163—164° (Found : C, 88·6; H, 4·5. Calc. for $C_{17}H_{10}O$ : C, 88·7; H, 4·4%), were obtained. These were identical with a specimen of 3 : 4-benzofluorenone, obtained by decarboxylation of 3 : 4-benzofluorenone-1-carboxylic acid with quinoline and copper bronze (Schaarschmidt, *loc. cit.*, decarboxylated the acid by dry distillation and gave 161° as the m. p. of 3 : 4-benzofluorenone).

$3:4$-*Benzo*-$1:2:10:11$-*tetrahydrofluorenone* (IV; R = H).—The acid (IV; R = $CO_2$H) (1 part) was heated for 2 hours at 240° with copper powder (0·5 part) and quinoline (3 vols.). After dilution with ether the copper was collected, and the quinoline removed by washing five times with 5N-hydrochloric acid. The ethereal solution was washed with dilute sodium hydroxide solution and dried, the solvent removed, and the tetrahydrofluorenone (IV; R = H) crystallised from ether–ligroin. trans($10:11$)-$3:4$-*Benzo*-$1:2:10:11$-*tetrahydrofluorenone* (IV; R = H) was obtained in slender prisms, m. p. 161—163° (Found : C, 86·9; H, 5·8. $C_{17}H_{14}O$ requires C, 87·2; H, 6·0%), from either the *trans*($10:11$)*trans*($1:10$)-form A or the *trans*($10:11$)*cis*($1:10$)-form C of the acid (IV; R = $CO_2$H). The cis($10:11$)-$3:4$-*benzo*-$1:2:10:11$-*tetrahydrofluorenone* (IV; R = H) was prepared as nodules, m. p. 131—134° (Found : C, 86·8; H, 5·9%), from the *cis*($10:11$)*cis*($1:10$)-form B of the acid (IV; R = $CO_2$H).