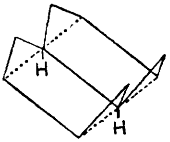
CCLVI.—*Studies in "Strainless" Rings. Part I. β-Substituted Stereoisomeric Decalins (Decahydronaphthalenes).*

By Keshaviah Aswath Narain Rao.

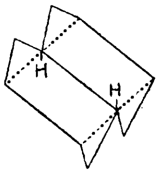
Considerable attention has in recent years been directed to the spatial arrangement of large monocyclic rings (Ruzicka, *Helv. Chim. Acta,* 1926, **9**, 499, etc.) and dicyclic rings (Windaus, Hückel, and Reverey, *Ber.*, 1923, **56**, 95; Hückel, *Nach. Ges. Wiss. Gottingen*, 1923, 43; *Annalen*, 1925, **441**, 1; 1927, **451**, 109; Hückel and Friedrich, *ibid.*, 1926, **451**, 132; Hückel and Stepf, *ibid.*, 1927, **453**, 163; Perkin and Sedgwick, J., 1924, **125**, 2437; 1926, 438; Perkin and Plant, J., 1927, 2676; Wightman, J., 1925, **127**, 1421;

1926, 2541), and the view is now more or less generally accepted that the strain caused by the distortion of the valencies in these rings is partly relieved in many cases by transformation from a uniplanar to a multiplanar system.

The theory of " strainless " rings was first advanced by Sachse (*Ber.*, 1890, **23**, 1363), who suggested that the strain in *cyclo*hexane is eliminated by the assumption of a multiplanar form. Since the isomerism demanded by this hypothesis has not been observed in the case of *cyclo*hexane and its derivatives (Wightman, *loc. cit.*), and there is other evidence (Beesly, Ingold, and Thorpe, J., 1915, **107**, 1080; see Ingold and Thorpe, J., 1928, 1320) indicating the presence of considerable strain in this ring, this hypothesis lacks experimental support. Mohr (*J. pr. Chem.*, 1918, **98**, 315; 1922, **103**, 316), who extended this idea and applied it to the case of dicyclic rings, postulated that the fusion of two strainless *cyclo*hexane rings to form decahydronaphthalene could take place by the union of either the *cis-* (I) or the *trans*-valencies (II), the latter being remarkable. The requirements of this theory with regard to isomerism have been brilliantly confirmed by Hückel and his collaborators. But the mere fact that these rings are capable of existing not only in *cis-* but also in *trans*-forms is in itself no proof of the absence of strain in them. The results from the heats of combustion have not been entirely satisfactory. The two *cyclo*hexane rings in decalin must obviously lie in different planes, but whether each or either of them is multiplanar and strainless can be decided only when further evidence of a different type is furnished (see Haworth, *Ann. Reports*, 1927, **24**, 98).



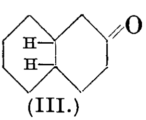
(I.)



(II.)

The " valency-deflexion " hypothesis of Thorpe and Ingold has been satisfied in its main demands by a large amount of experimental data. Evidence on diminished strain in *cyclo*heptane, obtained by a study of the *spiro*-compounds derived from it (Baker and Ingold, J., 1923, **123**, 122, etc.), is in harmony with that from other sources. This series of investigations is a study of the condition of strain in such dicyclic rings, and since decalin is the simplest of them, the preparation and properties of the stereoisomeric decalin-2 : 2-diacetic acids are now described.

Hückel (*Annalen*, 1927, **451**, 109) has already demonstrated the existence of four β-decalols (*cis*-, m. p. 105° and 17°; *trans*-, m. p. 75° and 53°) derived from the two β-decalones (III) and (IV).



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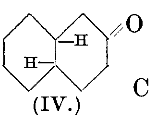
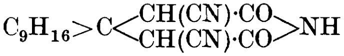
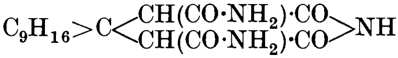


(IV.)



$$C_9H_{16}>C<\begin{matrix}CH(CN)\cdot CO\\ CH(CN)\cdot CO\end{matrix}>NH$$

(V.)



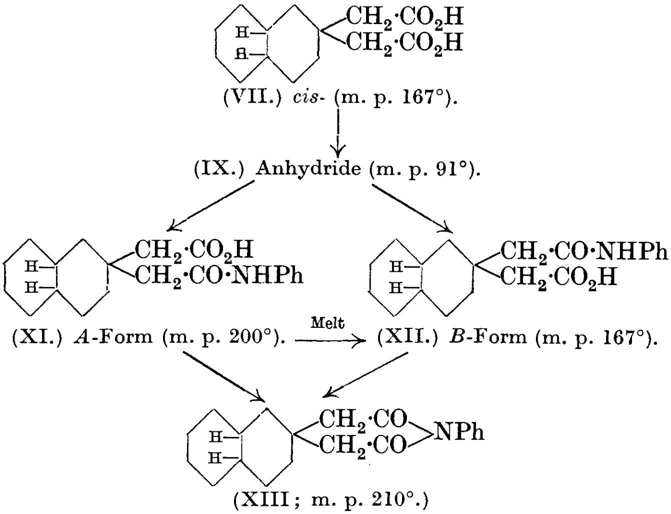
$$C_9H_{16}>C<\begin{matrix}CH(CO\cdot NH_2)\cdot CO\\ CH(CO\cdot NH_2)\cdot CO\end{matrix}>NH$$

(VI.)

cis- and *trans*-β-Decalones, prepared from the β-decalols of m. p. 105° and 75°, respectively, differ considerably in their tendency to condense with ethyl cyanoacetate and ammonia in ethyl-alcoholic solution according to Guareschi's method (Thole and Thorpe, J., 1911, **99**, 422; Kon and Thorpe, J., 1919, **115**, 686); for, under similar conditions, more than 70% of *trans*-imide (V) is formed, whilst the yield of the *cis*-isomeride rarely exceeds 40%. The reason for this contrast possibly lies in the difference in solubility between the ammonium salts of the *cis*- and *trans*-dicyano-imides in the alcoholic solution : the almost complete precipitation of the very sparingly soluble *trans*-compound would facilitate its production, and, on the other hand, the increased concentration of the freely soluble *cis*-isomeride would inhibit the progress of the reaction, resulting in a diminished yield. This divergence in their properties has made it possible to prepare the stereochemical individuals in a pure condition from a mixture of β-decalones.

Both the dicyano-imides give on treatment with cold concentrated sulphuric acid the *cis*- and *trans*-dicarbamyl-imides (VI), and are converted by complete hydrolysis with 60% sulphuric acid (Thole and Thorpe, *loc. cit.*; Kon and Thorpe, *loc. cit.*) into *cis*- (VII) and *trans*- (VIII) -decalin-2 : 2-diacetic acids.

The two diacetic acids resemble each other very closely in their properties. They are sparingly soluble in all the usual solvents except acetone and alcohol, do not crystallise well, and form insoluble metallic salts, thus differing markedly from the 1 : 1-diacetic acids of *cyclo*-pentane, -hexane, and -heptane. A mixture of the acids melts at an intermediate temperature, *viz.*, 167—169°, and this property, which is not infrequently displayed by compounds closely allied in structure, is also exhibited by the semicarbazones of the parent decalones (*cis*-, m. p. 185—186°; *trans*-, 193°; mixture, m. p. 185°). Since this close resemblance between the two acids extends to most of their derivatives, which are therefore classified into an (*A*) and a (*B*) series, identification of an acid of unknown parentage is difficult, and separation of a stereoisomeric mixture into its components has not been achieved.

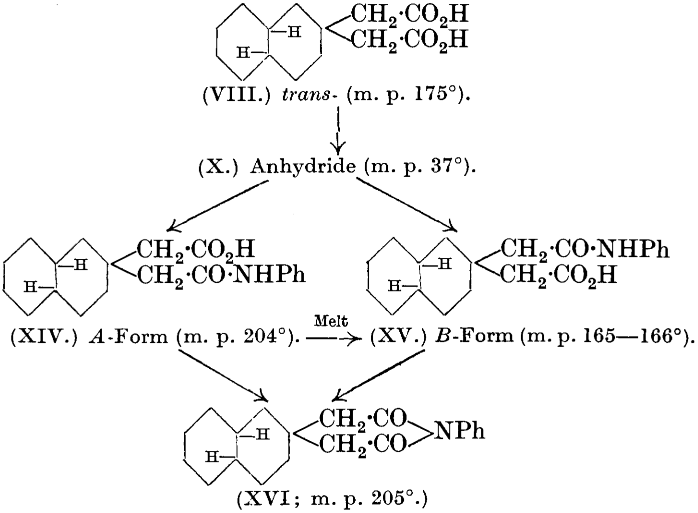


(VII.) *cis*- (m. p. 167°).

(IX.) Anhydride (m. p. 91°).

(XI.) *A*-Form (m. p. 200°). $\xrightarrow{\text{Melt}}$ (XII.) *B*-Form (m. p. 167°).

(XIII; m. p. 210°.)



(VIII.) *trans*- (m. p. 175°).

(X.) Anhydride (m. p. 37°).

(XIV.) *A*-Form (m. p. 204°). $\xrightarrow{\text{Melt}}$ (XV.) *B*-Form (m. p. 165—166°).

(XVI; m. p. 205°.)

Each of the *anhydrides* (IX) and (X) derived from the *cis*- and *trans*-acids gives a pair of *anilic acids*; the (*A*) anilic acids, (XI) and (XIV), are sparingly soluble and resemble each other closely in other properties, and the (*B*) acids, (XII) and (XV), do so to an even greater degree, melting at nearly the same temperature (*cis*-, 167°; *trans*-, 165—166°) and not depressing each other's melting point. The chemical individuality of *cis*- and *trans*-*B* anilic acids is, however, clearly demonstrated by the formation of different anils from them, for the cis-*anil* (XIII) prepared by melting either of the *cis*-anilic acids can be easily distinguished from the trans-*anil* (XVI) obtained by dehydration of the *trans*-anilic acids. Particular attention may be directed to the conversion of the less fusible (*A*) forms into the (*B*) compounds—a curious inversion of stability further emphasised by the formation of the latter from the anhydride to the greater extent (65%)—contrary to the well-established stability of the high-melting forms into which the more fusible isomerides are usually converted.

Comparison of the physical properties of the *ethyl* esters of (VII) and (VIII) shows the same relationship as has been found by Hückel (*Fortschritte der Chemie, Physik und Physikalischen Chemie*, Bd. 19, Heft 4, 1927, 45) in the case of other liquid isomerides. The *cis*-isomeride has usually a higher b. p., density, and refractive index, but a lower molecular refraction than the *trans*-form, thus :

Ethyl ester of	(VII).	(VIII).
B. p.	213°/21 mm.	209°/16 mm.
Density	$d_{4°}^{18·8°}$ 1·04874	$d_{4°}^{16·8°}$ 1·04115
Refractive index	$n_{D}^{18·8°}$ 1·47918	$n_{D}^{16·8°}$ 1·47702
$[R_L]_D$ (Calc., 84·23)	83·85	84·14

Ethyl *trans*-decahydronaphthylidene-2-cyanoacetate (XVII), prepared by condensing *trans*-β-decalone with ethyl cyanoacetate in presence of piperidine, displays a considerable preponderance of

$C_9H_{16}{>}C{=}C(CN){\cdot}CO_2Et$ (XVII.)

$C_9H_{15}{>}C{-}CMe(CN){\cdot}CO_2Et$ (XVIII.)

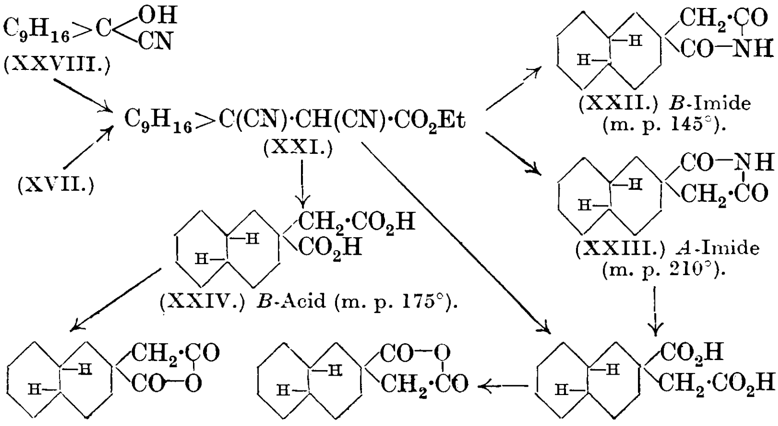
(XIX.) $C_9H_{15}{>}C{-}CH_2{\cdot}CN$

$C_9H_{16}{>}C{=}CMe{\cdot}CN$ (XX.)

the αβ-phase as shown by its ready addition of polar reagents like potassium cyanide with formation of metallo-derivatives, its disinclination to react with bromine, its oxidation into *trans*-β-decalone, and its conversion into the *trans*-dicyano-imide (V) on condensation with another molecule of ethyl cyanoacetate. In this respect, it behaves very similarly to ethyl *cyclo*hexylidenecyanoacetate, which has been shown by Lapworth and McRae (J., 1922, **121**, 2741) and by Birch, Kon, and Norris (J., 1923, **123**, 1369) to react chiefly in the αβ-phase. Like the latter substance, it can, however, be methylated to form (XVIII), thus demonstrating the presence of the βγ-phase in the tautomeric mixture. A comparison of the optical properties of the methylated ester, where the βγ-form is alone possible, with that of the parent ester further emphasises the type of unsaturation in the latter. In accordance with its structure, (XVIII) reacts rapidly with bromine and is insoluble in a solution of potassium cyanide.

The *nitrile* (XIX), formed on distillation of the liquid cyano-acid obtained by the hydrolysis of (XVII), is probably a βγ-isomeride, as has been found in the case of other unsaturated nitriles prepared from cyano-acids (Dr. A. Kandiah, private communication). The methylated *nitrile* (XX), prepared by removal of the carbethoxy-group from (XVIII), shows exaltation in its molecular refraction, in agreement with the observations of Birch and Kon (J., 1923, **123**, 2442) in the case of analogous nitriles, and is probably an αβ-isomeride. Whether the double bond in the methylated derivatives lies in position 1 : 2 or 2 : 3 remains undecided.

With the intention of preparing the stereoisomeric 2-carboxy-*trans*-decalin-2-acetic acids, Hückel and Wiebke (*Ber.*, 1926, **59**, 2843) condensed *trans*-2-ketodecahydronaphthalene cyanohydrin (XXVIII) with ethyl sodiocyanoacetate according to Higson and Thorpe (J., 1906, **89**, 1455). By the hydrolysis of the resulting dicyano-ester (XXI), they obtained a liquid acid from which they isolated a small quantity of solid, m. p. 149—150°. This has been described as *pure* 2-carboxy-*trans*-decalin-2-acetic acid and characterised by its anhydride, m. p. 91°. In the present instance, the unsaturated cyano-ester (XVII) has been found to condense smoothly with potassium cyanide in alcoholic solution to form the dicyano-ester (XXI), which on complete hydrolysis with sulphuric acid gives a liquid acid. This, after purification through the ester and trituration with ether–light petroleum, readily yields a small quantity of a solid. This acid, m. p. 197°, has been shown to be


$C_9H_{16}{>}C{<}^{OH}_{CN}$ (XXVIII.)

$C_9H_{16}{>}C(CN){\cdot}CH(CN){\cdot}CO_2Et$ (XXI.)

(XVII.)

(XXII.) *B*-Imide (m. p. 145°).

(XXIII.) *A*-Imide (m. p. 210°).

(XXIV.) *B*-Acid (m. p. 175°).

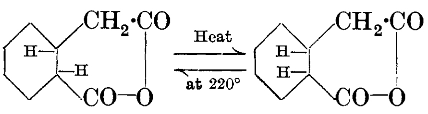
(XXV; m. p. 98°). (XXVII; m. p. 94°). (XXVI.) *A*-Acid (m. p. 197°).

one of the two theoretically possible 2-carboxy-*trans*-decalin-2-acetic acids and may be called the (*A*) form (XXVI). The non-solidifying residue remaining after removal of the (*A*) acid partly crystallises on conversion into the anhydride and distillation. The (B) *acid* (XXIV), formed on decomposing the crystalline anhydride (m. p. 98°), melts at 175°. It is therefore obvious that the 2-carboxy-*trans*-decalin-2-acetic acid and its anhydride described by Hückel and Wiebke are mixtures of the (*A*) and (*B*) forms.

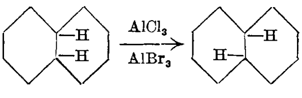
On partial hydrolysis with sulphuric acid, (XXI) gives a mixture of imides, which can be separated by fractional crystallisation into two compounds, (i) the (*B*) *imide* (XXII), m. p. 145°, and (ii) the (*A*) *imide* (XXIII), m. p. 210°, the latter being converted by hydrolysis with potassium hydroxide into the (*A*) acid (XXVI).

These results are completely in agreement with Mohr's theory. Substituted *cis*- and *trans*-decalins of the type $C_9H_{16}{>}C{<}^{X}_{Y}$ are capable of existing in four forms (the anilic acids). When, however, X and Y are identical (as in the diacetic acids), only one isomeride corresponding to each decalin is formed, the same result being achieved by replacing X and Y by a symmetrical ring (the anhydrides and anils). There is one point of interest, however, to which attention may be directed, *viz.*, the replacement of the dissimilar groups X and Y by an unsymmetrical ring does not diminish the number of isomerides. This can be the only explanation of the existence of the two imides (XXII) and (XXIII), and the anhydrides (XXV) and (XXVII).

It is improbable that there is a change of nuclear configuration during the hydrolysis of the dicyano-ester (XXI). It is true that isolated instances of *cis-trans* conversion in this type of substance have been recorded : Windaus, Hückel, and Reverey (*loc. cit.*) converted *cis*- and *trans*-anhydrides of hexahydrohomophthalic acid, (XXIX) and (XXX), into a mixture of the two; and *cis*-decalin (XXXI) was converted into *trans*-decalin (XXXII) on heating with aluminium chloride or bromide (Zelinski and Turowa-Pollak, *Ber.*, 1925, **58**, 1298; Hückel, *loc. cit.*); but the fundamental postulate of Mohr allows of no such interconversion ordinarily. The two rings lock each other in such a way that, although variation of each formula can be produced by twisting or simultaneous rotation, no interconversion can take place except by the temporary rupture of one of the bonds (see Ingold, *Ann. Reports*, 1924, **21**, 92; Hückel, *loc. cit.*). The *cis*- and *trans*-compounds would consequently be stable isomerides, and this is exactly what has been



(XXX.) (XXIX.)



(XXXI.) (XXXII.)

observed in the experiments now recorded : in no instance has interconversion by melting, distillation, or boiling with acids or alkalis been observed. There is no reason, therefore, to believe that the two acids (XXIV) and (XXVI) do not possess the same nuclear configuration. It is intended, however, to confirm this conclusion by the synthesis of the acids from *cis*-β-decalone, when this becomes available.

EXPERIMENTAL.

trans-*Series.*

trans-β-*Decalone* (IV).—To a solution of *trans*-β-decalol, m. p. 75° (50 g.), in glacial acetic acid (150 c.c.), was added a concentrated aqueous solution of chromic acid (26 g.) portionwise and the solution was kept for 48 hours. As the ketone distilled very slowly in steam, Hückel's method (*Nach. Ges. Wiss. Gottingen*, 1923, 43; *Annalen*, 1925, **441**, 1) was not suitable for its preparation in bulk, and the oxidation mixture was therefore heated on the steam-bath for a few hours, diluted with water, the excess of acetic acid partly neutralised, and the precipitated oil thoroughly extracted with ether. Purified through the sodium bisulphite compound, *trans*-β-decalone had b. p. 117°/16 mm. (semicarbazone, m. p. 193° on slow heating), $d_{4^\circ}^{22 \cdot 2^\circ}$ 0·97624, $n_{\mathrm{D}}^{22 \cdot 2^\circ}$ 1·48337 (Hückel gives b. p. 126°/30 mm., semicarbazone, m. p. 192—193°, $d_{4^\circ}^{20^\circ}$ 0·975, $n_{\mathrm{D}}^{19^\circ}$ 1·48088).

Condensation of trans-β-*Decalone with Ethyl Cyanoacetate : ω-Imide of* trans-*Decahydronaphthalene*-2 : 2-*dicyanoacetic Acid* (V).—Absolute alcohol (500 c.c.) cooled in a freezing-mixture was saturated with ammonia, mixed with ice-cold *trans*-β-decalone (152 g.) and ethyl cyanoacetate (226 g.) in a stoppered bottle, and kept for a week. The large quantity of the ammonium salt of the dicyano-imide which had been precipitated was filtered off, decomposed by boiling with dilute hydrochloric acid, thoroughly washed with boiling water, and dried at 100° (164 g.). The unchanged ketone precipitated on diluting the filtrate with water having been removed with ether, a further quantity of the dicyano-imide (6 g.) was obtained (total yield 60%). If the reaction mixture was kept for a month, the yield was increased to 74%.

Very sparingly soluble in all solvents, the *ω-imide* of trans-*decahydronaphthalene*-2 : 2-*dicyanoacetic acid* crystallises best from ethyl alcohol, separating in silky needles, or from acetone in colourless, lustrous, rectangular plates, m. p. 280° (decomp.) (Found : N, 14·4. $C_{16}H_{19}O_2N_3$ requires N, 14·7%).

ω-Imide of αα′-Dicarbamyl-trans-*decahydronaphthalene*-2 : 2-*diacetic Acid* (VI).—A solution of the above dicyano-imide in ten times its weight of sulphuric acid was kept for 24 hours and then poured on ice. After several crystallisations from ethyl alcohol, the *dicarbamyl-imide* melts at 234—235° (Found : C, 59·5; H, 7·4. $C_{16}H_{23}O_4N_3$ requires C, 59·8; H, 7·2%).

trans-*Decahydronaphthalene*-2 : 2-*diacetic Acid* (VIII).—A solution of the dicyano-imide (100 g.) in concentrated sulphuric acid (420 c.c.) was kept for 24 hours, then diluted with water (90 c.c.) and heated *gently* for 3 hours on a sand-bath. The dark brown liquid was cooled, further diluted with water (300 c.c.), boiled for 6 hours, cooled in ice, and diluted, and the precipitate was collected after 6 hours. The acid was separated from any unchanged imide by extraction with dilute potassium carbonate solution (the sodium salt is too sparingly soluble), and purified through the ester or anhydride (yield 70 g.). Sparingly soluble in chloroform, benzene, and light petroleum, and moderately easily soluble in ether and alcohol, trans-*decahydronaphthalene*-2 : 2-*diacetic acid* crystallises from acetone in short colourless needles, m. p. 175° (sintering at 165°) (Found, after drying at 100° : C, 65·9; H, 8·8; equiv., by titration with baryta, 126·9. $C_{14}H_{24}O_4$ requires C, 66·1; H, 8·6%; equiv., 127). The acid is unchanged by boiling with 25% potassium hydroxide solution, concentrated hydrochloric or hydrobromic acid, or bromine.

The *methyl* ester, prepared by refluxing the acid (75 g.), methyl alcohol (400 c.c.), and sulphuric acid (60 c.c.) for 3 hours, boils at 190°/12 mm. (Found : C, 67·7; H, 9·1. $C_{16}H_{26}O_4$ requires C, 68·0; H, 9·2%). The physical constants of the *ethyl* ester (Found : C, 69·4; H, 9·8. $C_{18}H_{30}O_4$ requires C, 69·7; H, 9·7%) are given on p. 1958. Both esters are converted into the original acid on hydrolysis.

The *imide* is formed when the dicyano-imide is incompletely hydrolysed and is found in the residue after the acid has been extracted with potassium carbonate; it crystallises from dilute acetic acid or aqueous acetone in colourless plates, m. p. 201° (Found : N, 6·3. $C_{14}H_{21}O_2N$ requires N, 6·0%).

Di-p-*toluidide*. A molten mixture of the *trans*-diacetic acid and *p*-toluidine was kept for an hour at 200°; the unchanged base and acid having been removed, the trans-*di*-p-*toluidide* was crystallised from ethyl alcohol; m. p. 191° (sintering at 180°) (Found : C, 77·7; H, 8·3. $C_{28}H_{36}O_2N_2$ requires C, 77·8; H, 8·4%).

Anhydride (X). The acid (50 g.) was refluxed with acetyl chloride for 1 hour, and the latter then removed; the trans-*anhydride*, b. p. 240°/20 mm., is a thick viscous liquid, which, on long standing in a vacuum over potassium hydroxide, solidifies into a paraffin-like solid, m. p. 37° (Found: C, 71·3; H, 8·6. $C_{14}H_{20}O_3$ requires

C, 71·2; H, 8·5%). It can also be prepared by treating the acid with acetic anhydride or by distilling it under reduced pressure.

Isomeric Anilic Acids from trans-*Decahydronaphthalene*-2 : 2-*diacetic Acid.*—The anhydride was mixed with excess of aniline in benzene solution, and the solid collected after 24 hours; it melted indefinitely at 120—180°, and was separated by fractional crystallisation from aqueous acetone into two anilic acids: (1) the more soluble (XV), m. p. 159—161° (65%), and (2) the less soluble (XIV), m. p. 199° (35%).

(1) The stable trans-*anilic acid* (B) (XV) separates from benzene–light petroleum (b. p. 60—80°) in colourless needles and rectangular plates (dimorphous), which melt at 159—161°; by 24 hours' standing in a vacuum over concentrated sulphuric acid, the m. p. is raised to 165—166° (Found: C, 73·0; H, 8·2. $C_{20}H_{27}O_3N$ requires C, 73·0; H, 8·2%).

(2) The unstable trans-*anilic acid* (A) (XIV) crystallises from acetone in colourless, lustrous, rectangular plates, m. p. 204° (Found: C, 73·0; H, 8·3%). When it was kept molten at 210—220° for 15 minutes and extracted with dilute ammonia, the solid precipitated on acidification of this solution melted after recrystallisation at 165—166°, and was found to be identical with the stable acid (*B*) (XV).

Anil (XVI).—When either of the anilic acids was kept at 210—220° until evolution of water ceased (30 mins.), cooled, triturated with dilute ammonia to remove any unchanged acid, and twice crystallised from alcohol, the same trans-*anil* separated in short, colourless needles, m. p. 205° (Found: C, 77·1; H, 7·9. $C_{20}H_{25}O_2N$ requires C, 77·1; H, 8·1%). This anil could not be converted into the *cis*-isomeride (XIII).

Condensation of trans-β-*Decalone with Ethyl Cyanoacetate: Ethyl* trans-*Decahydro*-β-*naphthylidenecyanoacetate.**—A mixture of *trans*-β-decalone (112 g.), ethyl cyanoacetate (76 g.), and a few drops of piperidine was kept for 3 days and then heated on the steam-bath for 8 hours. The oil precipitated on dilution was extracted by ether, the extract washed with dilute hydrochloric acid and dried, and the ether removed. The residue distilled at 206—210°/14 mm. (105 g.), a mixture of unchanged ketone and ethyl cyanoacetate passing over at 120—126°/14 mm. On redistillation, pure ethyl *trans*-decahydro-β-naphthylidenecyanoacetate boils at 208°/14 mm. (Found: C, 72·7; H, 8·6. Calc. for $C_{15}H_{21}O_2N$: C, 72·9; H, 8·5%), and has $d_{4°}^{18·4°}$ 1·06067, $n_{D}^{18·4°}$ 1·51299, whence $[R_L]_D$ 70·04 (calc., 68·08). It is a highly viscous liquid and does not solidify in a

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* The properties of this substance were described by Vogel (J., 1928, 2026). Its initial preparation was due to the author.—J. F. T.

freezing mixture; it adds on bromine very slowly with gradual evolution of hydrogen bromide, and is soluble in an alcoholic solution of potassium cyanide. Oxidised with ice-cold potassium permanganate solution (1%), it gives *trans*-β-decalone, identified by means of its semicarbazone.

Condensation of the Foregoing Ester with Ethyl Cyanoacetate.—The unsaturated cyano-ester (12 g.), mixed with ethyl cyanoacetate (5·7 g.) and absolute ethyl alcohol (25 c.c.) saturated with ammonia, was kept for 2 days; the precipitated solid was isolated in the usual way (see p. 1961) and identified as the *trans*-dicyano-imide (V), m. p. 280° (10 g.).

Methylation of Ethyl trans-*Decahydro*-β-*naphthylidenecyanoacetate.*—The deep red colour produced when the unsaturated cyano-ester (XVII) (20 g.) was added to a solution of sodium (1·9 g.) in ethyl alcohol (30 c.c.) quickly disappeared, and methyl iodide (20 g.) was then added to the pale yellow solution. The mixture having been heated at 90° for 45 minutes, the oil precipitated on addition of water was extracted with ether, washed, dried, and distilled after removal of the solvent. On redistillation, pure *ethyl* α-*cyano*-α-$\Delta^{2:3(1:2)}$-trans-*decahydronaphthalene*-2-*propionate* (XVIII) boils at 192°/17 mm. (Found : C, 73·4; H, 8·8. $C_{16}H_{23}O_2N$ requires C, 73·6; H, 8·8%), and has $d_{4^\circ}^{18\cdot4^\circ}$ 1·03663, $n_D^{18\cdot4^\circ}$ 1·49098, whence $[R_L]_D$ 72·97 (calc., 72·69). It adds on bromine rapidly in chloroform solution (but no solid bromide could be isolated) and is insoluble in a solution of potassium cyanide.

$\Delta^{2:3(1:2)}$-trans-*Decahydronaphthalene*-2-*acetonitrile* (XIX).—The cyano-ester (XVII) (10 g.), mixed with a solution of sodium (1 g.) in methyl alcohol (40 c.c.), was refluxed for 1·5 hours, then diluted, and the unchanged ester extracted with ether. On acidifying the aqueous solution, the unsaturated cyano-acid, $C_9H_{16}{>}C{:}C(CN){\cdot}CO_2H$, was precipitated and extracted with ether. The residue obtained on removal of the dried ether could not be induced to crystallise, but solidified when cooled in ice. On distillation under reduced pressure it decomposed, and the portion of b. p. 150—170°/35 mm. was collected. After two distillations, the pure *nitrile* boiled at 164°/26 mm. (Found : N, 8·1. $C_{12}H_{17}N$ requires N, 8·0%).

α-trans-*Decahydronaphthylidene*-2-*propionitrile* (XX).—The methylated ester (XVIII) (8 g.) was mixed with a solution of sodium in ethyl alcohol (20 c.c.) and kept at 35° for 4 hours. The oil precipitated on dilution was extracted with ether, washed with water, and dried, and the ether removed. The residue distilled at 160—180°/39 mm. and no product of higher boiling point was found, thus indicating the complete removal of the carbethoxy-group under the experimental conditions. Pure α-trans-*decahydro*-

naphthylidene-2-propionitrile boils at 170—172°/18 mm. (Found : C, 81·7; H, 10·3; N, 7·2. $C_{13}H_{19}N$ requires C, 82·5; H, 10·3; N, 7·4%), and has $d_{4^\circ}^{19\cdot6^\circ}$ 0·9802, $n_D^{19\cdot6^\circ}$ 1·51245, whence $[R_L]_D$ 57·9 (calc., 57·19).

2-*Carboxy*-trans-*decahydronaphthalene*-2-*acetic Acids* (XXIV and XXVI).—Ethyl α-cyano-*trans*-decahydronaphthylidene-2-acetate (42 g.) in 95% ethyl alcohol (200 c.c.) was mixed with potassium cyanide (25 g.) dissolved in water (53 c.c.); there was immediate evolution of heat and crystals soon separated. After 3 days, the alcohol was removed and the tarry residue of dicyano-ester (XXI) was cautiously mixed with 300 c.c. of 75% sulphuric acid and heated gently for 1 hour. A further 88 c.c. of water were added to the cooled solution, which was then boiled for 4 hours. Ether extracted the oil precipitated on diluting the solution, the acid constituent of the oil being isolated by extraction with dilute sodium carbonate solution and reprecipitation. The thick, heavy oil thus precipitated was extracted with ether, the solution dried, and the ether removed. The residue showed no tendency to crystallise on standing for several days, and was therefore esterified with ethyl alcohol and sulphuric acid in the usual way. The *ethyl* ester boils at 200°/18 mm. (Found : C, 68·7; H, 9·6. $C_{17}H_{28}O_4$ requires C, 68·9; H, 9·5%), and has $d_{4^\circ}^{20\cdot5^\circ}$ 1·04947, $n_D^{20\cdot5^\circ}$ 1·47594, whence $[R_L]_D$ 79·73 (calc., 79·61). During the esterification a considerable quantity of the ethyl hydrogen ester is obtained, and this gives the same acid as the normal ester when submitted to the following treatment.

2-*Carboxy*-trans-*decahydronaphthalene*-2-*acetic acid* (A) (XXVI), m. p. 197°. The ethyl ester was hydrolysed by a few minutes' boiling with 50% potassium hydroxide solution, and the acid precipitated on acidifying the solution was extracted by ether. The extract was dried and the ether removed; the heavy viscous oil obtained, which did not show any signs of crystallisation on standing for several days, was triturated with a mixture of dry ether and light petroleum (b. p. 40—60°), and after a few hours a soft, colourless, crystalline powder was obtained. This crystallised from aqueous acetone in colourless, lustrous needles (Found : C, 65·0; H, 8·4; equiv., 120. $C_{13}H_{20}O_4$ requires C, 65·0; H, 8·4%; equiv., 120), which sinter at 185° and melt at 197° with violent effervescence and formation of anhydride. The (*A*) *acid* is insoluble in petroleum, sparingly soluble in chloroform and benzene, and moderately soluble in ethyl acetate, and is recovered unchanged after boiling with potassium hydroxide or hydrobromic acid for 3 hours.

Anhydride (A) (XXVII). The acid (*A*) (1 g.) dissolved in acetic anhydride (3 c.c.) was refluxed for 1 hour. The needles obtained on removal of the solvent crystallised from light petroleum (b. p. 60—

80°) in clusters of lustrous needles, m. p. 94° (Found : C, 70·2 ; H, 8·1. $C_{13}H_{18}O_3$ requires C, 70·3 ; H, 8·2%). The trans-*anhydride* (A) distils unchanged and shows no tendency to form the (*B*) isomeride. On treatment with a solution of sodium hydroxide or boiling with water for a long time, it is reconverted into the (*A*) acid, m. p. 197°.

The *anilic acid* (A) is precipitated within a few minutes when the (*A*) anhydride and aniline are mixed in benzene solution; after crystallisation from aqueous acetone, it has m. p. 193° (sintering at 180°) (Found : C, 72·7; H, 7·9. $C_{19}H_{25}O_3N$ requires C, 72·3; H, 8·0%). The trans-*anil* (A), prepared by heating the anilic acid (*A*) at 200° for 15 minutes, crystallises from ethyl alcohol in colourless needles, m. p. 166—167° (Found : C, 76·9; H, 7·6. $C_{19}H_{23}O_2N$ requires C, 76·8; H, 7·7%).

The (A) trans-*di*-p-*toluidide* crystallises from ethyl alcohol in soft, lustrous needles, m. p. 171° (Found : C, 77·0; H, 8·1. $C_{27}H_{34}O_2N_2$ requires C, 77·5; H, 8·2%).

2-*Carboxy*-trans-*decahydronaphthalene*-2-*acetic acid* (B) (XXIV), m. p. 175°. The thick viscous residue, from which as much of the (*A*) acid as possible had been removed by repeated treatment with ether and light petroleum, was boiled with acetic anhydride (20 g.) and then distilled under reduced pressure. After the acetic anhydride had passed over completely, the trans-*anhydride* (B) distilled at 197—220°/11 mm. It partly crystallised on standing for a few hours, and when purified by removal of the adhering oil by light petroleum (b. p. 40—60°) had m. p. 93°; recrystallisation from light petroleum gave lustrous rhombic plates, m. p. 98° [mixed m. p. with anhydride (*A*), 70°] (Found : C, 70·1; H, 8·3%). When the anhydride was decomposed with dilute potassium hydroxide solution it gave a crude acid of m. p. 170—173°. 2-*Carboxy*-trans-*decahydronaphthalene*-2-*acetic acid* (B) crystallises best from aqueous acetone, separating in stout needles and rectangular plates (dimorphous), m. p. 175° (sintering at 160°) [mixed m. p. with acid (*A*), 150—160°] (Found : C, 65·0; H, 8·5%; equiv., 119·2).

The trans-*anilic acid* (B) separates from aqueous acetone in colourless needles and rectangular plates, m. p. 198° (sintering at 193°) [mixed m. p. with the (*A*) anilic acid, 175—180°] (Found : C, 72·2; H, 8·0%).

Imides of 2-*Carboxy*-trans-*decahydronaphthalene*-2-*acetic Acids* (A) *and* (B) (XXII and XXIII).—The dicyano-ester (XXI) (50 g.) was cautiously mixed with 60% sulphuric acid and boiled for 4 hours. It was then cooled, diluted, and the precipitated oil thrice extracted with ether. The ethereal solution was extracted with a dilute solution of sodium carbonate to remove any acid formed, and evaporated; a large quantity of a crystalline solid mixed with a little oil was obtained. The crystals were freed from the oil by washing with light petroleum (b. p. 40—60°) and separated by fractional crystallisation from aqueous acetone into two imides, (I) the less soluble imide (*A*), m. p. 206—208°, and (2) the more soluble imide (*B*), m. p. 140—142°, which was obtained by diluting the mother-liquors.

The trans-*imide* (A) (XXIII) was purified by two crystallisations from acetone, from which it separated in lustrous plates, m. p. 210° (Found : C, 70·9; H, 8·7. $C_{13}H_{19}O_2N$ requires C, 70·5; H, 8·7%); on hydrolysis with potassium hydroxide, it gave the (*A*) acid, m. p. 197°. The trans-*imide* (B) (XXII) crystallises from benzene in lustrous needles, and from aqueous acetone in needles and plates, m. p. 145° (Found : C, 70·3; H, 8·7%). Both the (*A*) and the (*B*) imide are soluble in concentrated solutions of potassium hydroxide.

trans-*Amic Acid* (B), $C_{10}H_{16}(CO_2H)(CH_2\cdot CO\cdot NH_2)$.—A solution of the imide (*B*) in 25% potassium hydroxide was boiled for a few minutes, and then diluted and acidified. The crystalline solid precipitated was separated into acid and neutral portions by treatment with sodium carbonate. The *amic acid* crystallised from aqueous acetone in pearly plates, m. p. 217° (sintering at 210°) (Found : C, 65·4; H, 8·6. $C_{13}H_{21}O_3N$ requires C, 65·3; H, 8·8%).

cis-*Series.*

cis-β-*Decalone.*—The pure ketone prepared by the oxidation of *cis*-β-decalol, m. p. 105°, boils at 119°/16 mm. (semicarbazone, m. p. 185—186°) and has $d_{4^\circ}^{18\cdot8^\circ}$ 1·00298, $n_D^{18\cdot8^\circ}$ 1·49366 (Hückel records b. p. 128°/26 mm., $d_{4^\circ}^{20^\circ}$ 1·0038, $n_D^{20^\circ}$ 1·49265; semicarbazone, m. p. 182—183°).

ω-*Imide of* cis-*Decahydronaphthalene*-2 : 2-*dicyanoacetic Acid* (V).—*cis*-β-Decalone (50 g.) was condensed with ethyl cyanoacetate and ethyl-alcoholic ammonia in the usual manner. After 2 weeks, there being no precipitate, the solution was diluted with water, and the unchanged ketone extracted with ether. The crimson solution was then acidified with dilute hydrochloric acid; it became pale yellow, and the precipitated crystals were collected after 12 hours (yield, 38 g.; 40%). Shorter periods of keeping gave somewhat lower yields (28—32%). The *cis*-dicyano-imide separates from dilute ethyl alcohol in minute crystals, m. p. 242—243° (decomp.) (Found : C, 67·0; H, 6·8%). Hückel and Wiebke (*Ber.*, 1926, **59**, 2842) give m. p. 238—239°, but do not record yields.

The ω-*imide* of αα′-*dicarbamyl*-cis-*decahydronaphthalene*-2 : 2-*diacetic acid* (VI) when crystallised from glacial acetic acid has m. p. 260—261° (decomp.) (Found : C, 55·3; H, 7·4. $C_{16}H_{23}O_4N_3$,1·5 $CH_3\cdot CO_2H$ requires C, 55·4; H, 7·1%).

cis-*Decahydronaphthalene*-2 : 2-*diacetic Acid* (VII).—Hückel and Wiebke found that sulphuric acid was not suitable for the hydrolysis of the above dicyano-imides, but the method by which they obtained the diacetic acids is ill adapted for the accumulation of the large quantities required for this investigation, and it was then found that the *cis*-dicyano-imide could be successfully hydrolysed with sulphuric acid under the same conditions as those employed in the case of the *trans*-isomeride.

cis-Decahydronaphthalene-2 : 2-diacetic acid was obtained in 62% yield and then purified through the ester; it is very sparingly soluble in chloroform, benzene, and light petroleum, but quite soluble in acetone and in methyl and ethyl alcohol, and crystallises best from aqueous acetone; m. p. 167° (mixed m. p. with *trans*-acid, 167—169°) (Found : C, 66·3; H, 8·7%; equiv., 127). It is more soluble in ether than the *trans*-isomeride. It was not possible to separate a mixture of *cis*- and *trans*-acids into its components by any of the usual methods.

Neutral solutions of the *cis*- and *trans*-acids give bluish-green precipitates with a solution of copper sulphate, and colourless precipitates with solutions of barium chloride, calcium chloride, lead acetate, and silver nitrate, all the precipitates being insoluble in boiling water.

The two diacetic acids and (*A*) and (*B*) 2-carboxy-*trans*-decahydronaphthalene-2-acetic acids, when heated with resorcinol and a few drops of concentrated sulphuric acid for a short time, diluted, and made alkaline, give crimson-red solutions which display intense green fluorescence.

Ethyl cis-*decahydronaphthalene*-2 : 2-*diacetate* (Found : C, 69·2; H, 9·6%) has the physical constants given on p. 1958. The *imide* crystallises from methyl alcohol in colourless needles (Found : C, 71·4; H, 9·2%), m. p. 205° (mixed m. p. with *trans*-isomeride, 180—185°).

The *anhydride* (IX) crystallises from benzene–light petroleum (b. p. 40—60°) in short, stout, colourless needles, which gradually change into thick plates massed together, and melts at 91° (Found : C, 70·8; H, 8·8%).

Anilic acids. The mixture of anilic acids obtained by treating the anhydride with aniline in benzene solution was fractionally crystallised from aqueous acetone.

(1) The more soluble, cis-*anilic acid* (B) (XII), after two crystallisations from benzene has m. p. 167° (sintering at 150°) (Found: C, 73·3; H, 8·4%), and does not depress the m. p. of the *trans*-acid (*B*) (XV).

(2) The less soluble, cis-*anilic acid* (A) (XI), on recrystallisation

from aqueous acetone, gives clusters of needles, m. p. 200° (sintering at 190°) (Found : C, 73·1; H, 8·4%); mixed with the *trans*-acid (*A*), it melts at 180—190°. When melted and maintained at 200° for a few minutes, it is converted into a mixture of (*A*) and (*B*) *cis*-acids.

The same cis-*anil* (XIII) is formed from either of the *cis*-anilic acids and after three crystallisations from acetone melts at 210° (Found : C, 77·1; H, 7·9%).

The cis-*di*-p-*toluidide* crystallises from ethyl alcohol in pearly plates (Found : C, 77·8; H, 8·6%), m. p. 204° (mixed m. p. with *trans*-isomeride, 180°).

β-*Decalols.*—Solid β-decalols could not usually be obtained, and when available were often found to be mixtures, m. p. 70—95°. The liquids supplied by Deutsche Hydrierwerke were usually thick and viscous, and sometimes partly crystallised on standing for several weeks. On fractional distillation, varying quantities (sometimes as much as 50%) of decalin, b. p. 80—120°/20 mm., were obtained before the decalol, b. p. 124—132°/18 mm. Neither the mixture of decalols nor that of the ketones obtained on oxidation could be separated into its components by the usual methods. The proportion of the *cis*- and *trans*-isomerides in the mixture varied, there being, however, always a preponderance of the latter.

For the preparation of pure *cis*- and *trans*-decalin-2 : 2-diacetic acids from a mixture of β-decalones, advantage was taken of the difference in solubility of the ammonium salts of the two dicyano-imides in ethyl alcohol. For example, β-decalone (500 g.) was condensed with the requisite amounts of ethyl acetate and alcoholic ammonia; after a week, the precipitated solid, which was filtered off and purified in the usual way (see p. 1961), had m. p. 265—275° (decomp.) and was found to be fairly pure *trans*-dicyano-imide (390 g.). The filtrate was kept for another 2 weeks, and the small quantity of precipitate (mixture of dicyano-imides, 12 g.) collected; the dicyano-imide in the solution was isolated according to the method described in the case of the *cis*-compound (p. 1967) and found to be fairly pure *cis*-dicyano-imide, m. p. 230—235° (65 g.). The yields of the two dicyano-imides correspond approximately to 80% of *trans*- and 20% of *cis*-β-decalone in the original mixture.

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