297. *Three-carbon Tautomerism in Dicyclic Systems. Part I. Comparison of Corresponding Compounds of* trans-β-*Decalin and* cyclo*Hexane.*

By R. S. Thakur.

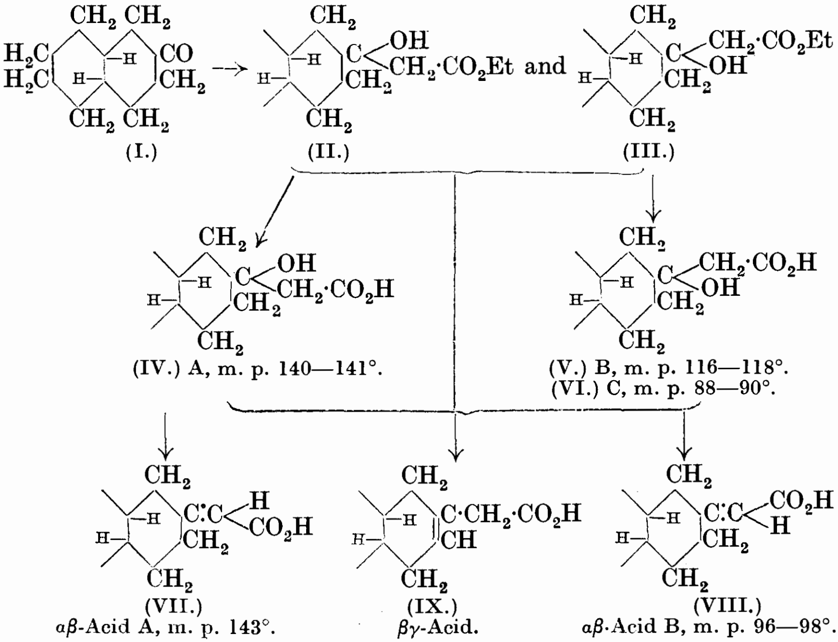
In their investigations of cyclic compounds of the type $(CH_2)_n{>}C{:}CHX$ ($n = 4$, 5, or 6; $X = CO_2H$, CO_2Et, COAlk, or CN) Kon, Linstead, and their collaborators observed some remarkable and theoretically unexpected differences amongst otherwise similar compounds: *e.g.*, whereas in a number of *cyclo*pentenyl derivatives the equilibrium is on the side of the αβ-form, in the *cyclo*hexenyl compounds it is on the side of the βγ; again, the former compounds are without exception much more mobile than the latter.

It is difficult to reconcile these facts with the theories based on the ionic-electromeric mechanism (Ingold, Shoppee, and Thorpe, J., 1926, 1497; Ingold, *Ann. Reports*, 1927, **24**, 106; Linstead, J., 1929, 2498) put forward to explain the effect of structure on tautomerism. The influence of ring strain was tentatively advanced by Kon and Speight (J., 1926, 2727; compare also Linstead, J., 1929, 2502) as an explanation, and it appeared to be of interest to pursue the matter further.

Attention has therefore been directed to dicyclic systems the strainless character of which is now generally accepted, and the behaviour of compounds containing a decahydronaphthalene ring has been compared with that of the corresponding *cyclo*hexane compounds, in which the existence of strain is by no means finally proved. *trans*-β-Decalol being easily obtainable in the pure form, the compounds of *trans*-β-decahydronaphthalene were synthesised for this purpose. An added interest attached to this choice, as the model of *trans*-β-decahydronaphthalene should be under considerable strain on the conception of inclined uniplanar component rings (Haworth, *Ann. Reports*, 1927, **24**, 99).

All the compounds depicted in the accompanying scheme have been isolated in the preparation of the unsaturated acids (VII) and (IX) from *trans*-β-decalone (I) (compare Rao, J., 1930, 1162). Ethyl 2-hydroxy-*trans*-decalin-2-acetate (II, III) seems to be a mixture, as it boils over a wide range and gives two fractions having different physical properties. By hydrolysis it yields three isomeric acids (mainly V; IV, VI): on the Sächse–Mohr hypothesis it is difficult to explain the existence of more than two, but (VI) may be a eutectic mixture of the other two.

More interesting is the isomerism observed in the acids obtained by the dehydration of the hydroxy-acids with acetic anhydride. The two *trans*-decahydronaphthylidene-2-acetic acids, to which the configurations (VII) and (VIII) are arbitrarily assigned, are distinct individuals, differing in m. p., in solubility, and in their derivatives, and their *ethyl* esters (X and XI; formulæ as VII and VIII, respectively), though having nearly the same physical properties, yield two distinct acids on hydrolysis, but on ozonolysis give the same ketone (I). The acid (VIII) is stable to boiling dilute hydrochloric acid and is only partly converted into (VII) and the βγ-acid (IX) by prolonged exposure to ultra-violet light: the conversion of (VII) into (VIII) by similar treatment was not observed. The two acids are converted into the same βγ-acid (IX) by



(I.) (II.) (III.)

(IV.) A, m. p. 140—141°.

(V.) B, m. p. 116—118°.
(VI.) C, m. p. 88—90°.

(VII.) αβ-Acid A, m. p. 143°.

(IX.) βγ-Acid.

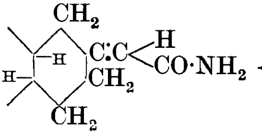
(VIII.) αβ-Acid B, m. p. 96—98°.

boiling alkali. This appears to be the first instance of the isolation of such a pair of cyclic acids, though their existence has long been suspected (compare Eccott and Linstead, J., 1929, 2153; Kon and Thakur, J., 1930, 2217; Kon, Leton, Linstead, and Parsons, J., 1931, 1411).

In the preparation of the αβ-acid under certain conditions, a considerable quantity of a neutral compound is isolated; this does not seem to be a lactone, but yields on distillation the βγ-acid (IX) and 2-*methylene*-trans-*decalin* (XIX). When the αβ-acid is itself heated with acetic anhydride in presence of pyridine, an analogous neutral compound is obtained, which gives the βγ-acid on distillation.

The constitution of the βγ-acid (IX) as the $\Delta^{2:3}$- and not the $\Delta^{2:1}$-acid, left undetermined by Rao (*loc. cit.*), has now been settled by the isolation of trans-*cyclo*hexane-1:2-diacetic acid from the product of ozonolysis of the βγ-ester (XII; formula as IX).

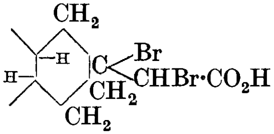
The acid chlorides of (VII) and (VIII) undergo extensive isomeric change on distillation (compare Newbery, J., 1925, **127**, 295; Johnson and Kon, J., 1926, 2648; Eccott and Linstead, J., 1929, 2153), but by working at a low temperature and avoiding distillation it has been possible to prepare the pure chlorides, and from them pure derivatives, *e.g.*, the two amides (XIII) and (XIV).



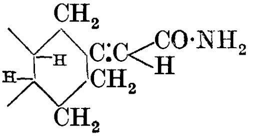
(XIII.) Amide A, m. p. 188°.

← αβ-Acid A →

(VII.)



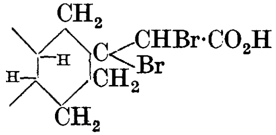
(XVI.) Dibromide A, m. p. 155°.



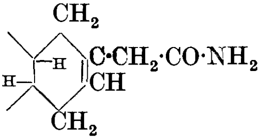
(XIV.) Amide B, m. p. 147°.

← αβ-Acid B →

(VIII.)



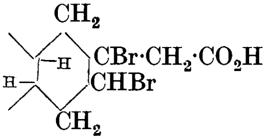
(XVII.) Dibromide B, m. p. 144°.



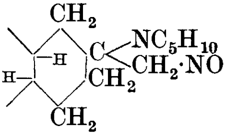
(XV.) βγ-Amide, m. p. 182°.

← βγ-Acid →

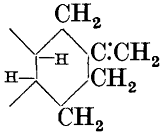
(IX.)



(XVIII.) βγ-Dibromide, m. p. 181°.



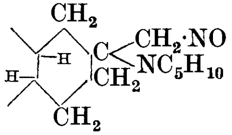
(XX.) Nitrolpiperidide A, m. p. 198° (decomp.).



(XIX.)

↓

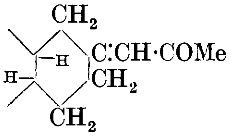
↖ Nitrosochlorides ↗
(not isolated)

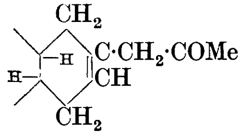


(XXI.) Nitrolpiperidide B, m. p. 154°.

Two *trans*-decahydronaphthylidene-2-acetones also should be obtainable from these acid chlorides by condensation with methylzinc iodide, but distilled acid chlorides were used in the syntheses and only one ketone (XXII) was isolated (*semicarbazone*, m. p. 187°). A small quantity of a second semicarbazone (m. p. 199°) was, however, obtained.

(XXII.)





(XXIII.)

The *ketone* (XXII) was also obtained, together with some of the βγ-isomeride (XXIII), by the Blaise–Maire reaction from the acid chloride of 2-hydroxy-*trans*-decalin-2-acetic acid (compare Kon and Narayanan, J., 1927, 1546): it had the molecular exaltation

(1·22) characteristic of such compounds and gave decalone on oxidation.

The synthesis of the pure αβ-ketone (XXII) presented great difficulty on account of the considerable conversion of the αβ-acid chloride into the βγ-form on distillation and the tendency of the semicarbazones of the αβ- and the βγ-isomeride to form a low-melting (80—98°) eutectic mixture containing the constituents roughly in the ratio in which the ketones are present at equilibrium. Attempts to break up this combination by treatment with dilute aqueous sodium hydroxide (Forster and Zimmerli, J., 1910, **97**, 2156), by differential hydrolysis with dilute sulphuric acid or oxalic acid, and by exposure to ultra-violet light (Heilbron and Wilson, J., 1912, **101**, 1482 ; *et seq.*) were all fruitless.

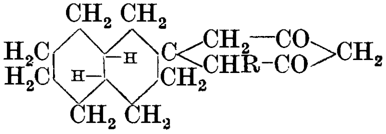
On the other hand, Δ^2-trans-*octahydronaphthyl-2-acetone* (XXIII) was readily obtained either by direct synthesis or by treatment of the ketone, regenerated from the crude semicarbazone, with aluminium amalgam (Harries and Eschenbach, *Ber.*, 1896, **29**, 380 ; Abbott, Kon, and Satchell, J., 1928, 2514).

A semicarbazone, m. p. 175°, obtained from the product of one of the Blaise–Maire reactions with the αβ-acid chloride was thought to be derived from the αβ-ketone (XXII), but the iodine addition and the physical properties of the regenerated ketone agreed with its βγ-structure. When, however, a ketone, regenerated from crude semicarbazone which had been exposed to ultra-violet light, was treated with aluminium amalgam, the product obtained gave the same semicarbazone, m. p. 175°, and an isomeride, m. p. 134°.

The condensation of decalone with acetone under Wallach's conditions (*Annalen*, 1912, **394**, 362) gave a very poor yield of the unsaturated ketones (XXII, XXIII). The semicarbazone (m. p. 96—98°) prepared from the product could not be resolved into its constituents and the ketone regenerated from it had the physical properties and iodine addition of the equilibrated ketone (see later). This is hardly surprising, since it was formed in the presence of a large excess of sodium ethoxide. The condensation by Grignard and Fluchaire's method (*Ann. Chim.*, 1928, **9**, 5) did not yield any better results.

An attempt to isolate the four stereoisomeric forms of the

(XXIV.)



dihydroresorcinol ester (XXIV ; R = CO_2Et) resulting from the condensation of the ketones with ethyl sodiomalonate (Norris and

Thorpe, J., 1921, **119**, 1199) was unsuccessful because the ester would not crystallise from any solvent; but only one form of the dihydroresorcinol derivative, *trans*-decahydronaphthalene-2-*spirocyclo*hexane-2′:6′-dione (XXIV; R = H), was obtained, as expected.

Tautomerism of the Acids (VII, VIII, IX), *Esters* (X, XI, XII), and *Ketones* (XXII, XXIII).

Acids.—A few experiments on the equilibration of the acids were carried out under Linstead's conditions (*loc. cit.*), but comparative values for their mobilities could not be determined on account of the incomplete dissolution of their potassium salts. A lower concentration of the catalyst (20% KOH) was therefore used to arrive at an approximate estimate. How incomplete dissolution of the potassium salts affects mobility can be gathered from the following figures :

	% KOH.	Hours.	Temp.	% Change.	Mobility
(1)	20	50	100°	24	0·06*
(2)	25	50	100	12	0·03
(3)	25	48	b. p.	66	0·3

* Half-change period 107 hours approx.

In (1) and (3), the potassium salt dissolved completely at the stated temperatures, whereas in (2) some was left undissolved. In (3), the effect of temperature is also superimposed.

The mobility of the αβ-acid B (VIII) was not determined. As the tautomeric change was very slow under the standard conditions, the point of equilibrium was determined with boiling alkali and the same value, 12 ± 1% of αβ-acid, was arrived at from all the acids.

No αβ-acid B, but only the βγ-acid (IX) and the αβ-acid A (VII) were isolated from the equilibration product of the acid B by the method of partial esterification (Thomas and Sudborough, J., 1911, **99**, 2307; Eccott and Linstead, J., 1929, 2153). No attempt was made to determine whether the geometrical inversion between the acids (VII and VIII) proceeds more rapidly than the tautomeric change (compare Linstead and Mann, J., 1931, 726). The formation of the acid A (VII) from the acid B (VIII) can take place (1) directly, (2) indirectly through the βγ-acid, or by both (1) and (2),

$$\begin{tikzcd} \alpha\beta\text{-B} \arrow[r] \arrow[dr] & \beta\gamma\text{-acid} \arrow[d] \\ & \alpha\beta\text{-A} \end{tikzcd}$$

but it is certain that the change βγ-acid ⟶ αβ-acid gives only the acid A (VII).

Brief reference may be made here to the effect of ultra-violet light on these acids in chloroform solution. Although no βγ-acid as such was isolated from the products, their iodine additions show definitely that tautomeric change, though extremely slow, does take place.

Esters.—The equilibration of the esters with sodium ethoxide (Kon and Linstead, *loc. cit.*) presented some points of interest on account of the geometrical isomerism of the αβ-esters (X, XI). Although the same equilibrium value is obtained for both esters, there is a marked difference in their rates of equilibration, as the following figures show (the βγ-ester being also included) :

Ester.	Mobility, $10^4 \times (k_1+k_2)$ min.$^{-1}$.	$t_{\frac{1}{2}}$.	Eqlm., % βγ.
αβ-A	6·9	17·5 hrs.	60
αβ-B	3·9	27 ,,	60
βγ	6·2	20 ,,	60

Nearly the same value (65% βγ) was obtained when the experiments were conducted at 100°, although a much shorter time was required.

No formation of the ethoxy-ester (compare Kon and Linstead, *loc. cit.*) was observed in the present study, but there was considerable hydrolysis in certain experiments. The composition (% βγ-acid) of the acid product can always be determined iodometrically and it has been found that the rate of hydrolysis of the βγ-ester is much greater than that of the αβ-ester (compare Kon and Linstead, *loc. cit.*) so that there is a drain of the former from the equilibrium mixture which causes a false increase in the αβ-content. In some of these cases it is possible to estimate the point of equilibrium by taking into account the quantity and composition of the mixture of acids formed. Such an estimate is justifiable because it has been shown that the sodium salts of the unsaturated acids formed as the result of hydrolysis do not undergo interconversion under the conditions of the experiment (Linstead, J., 1929, 2498) and therefore quantitatively represent the esters from which they are derived.

Thus, if some of the results in the present work are calculated in the light of these considerations, the apparent anomalies are seen to disappear and the following values are obtained :

Val. obs.	39	43	54% βγ
Val. calc.	64	62	60 ,,

Value at equilibrium 60% βγ.

Ketones.—Prolonged treatment of the αβ- and the βγ-ketone (XXII, XXIII) with sodium ethoxide seems to be accompanied by the addition of alcohol to the double bond, as the figures in the last column (p. 2137) show—a view confirmed also by the fall in the value of refraction with the seeming increase in αβ (?) content. But the equilibrium value and the mobility—35% βγ-ketone, $10^4(k_1 + k_2)$ min.$^{-1}$ = 800, with a half-change period of 8 minutes—which are determined from the βγ-side, can be regarded as trustworthy (Kon and Linstead, *loc. cit.*), especially when the time of treatment with the reagent is only 30 minutes.

An unusual result was obtained in attempting the equilibration of the ketone (regenerated from a eutectic mixture of semicarbazones, m. p. 96—98°) with sodium *iso*propoxide on the steam-bath. No ketonic fraction was obtained, but a considerable quantity of *trans*-β-decalol slowly separated from the distillate. A similar effect has been observed on pure *trans*-β-decalone itself in presence of dry sodium ethoxide, 28% of *trans*-β-decalol being isolated.

These results are tabulated below; values for the corresponding monocyclic derivatives $(CH_2)_n{>}C{:}CHX$ are included for comparison.

TABLE I.

	trans-β-$C_9H_{16}{>}$.	$n = 5$.	$n = 4$.	$n = 6$.	$n = 5$.		
					2-Me.	3-Me.	4-Me.
X = CO_2H.							
Eqlm. % αβ	12 ± 1	12[1]	14[3]	28[5]	11·5[6]	9[6]	7[6]
Mobility	0·05	1	22	0·66	0·15	0·27	0·42
Half-change (hrs.)	107	8	42	—	50	26	17
X = CO_2Et.							
Eqlm. % αβ	40	38[2]	60[7]	—	—	—	—
Mobility	6	8·1	835	—	—	—	—
Half-change (hrs.)	20	14·1	8·5 mins.	—	—	—	—
X = COMe.							
Eqlm. % αβ	35	23[2]	77[4]	60[5]	0[6]	25[6]	20[6]
Mobility	800	700	3000	3500	—	—	700
Half-change (mins.)	8	10	—	<2	—	—	—

[1] Linstead, J., 1927, 2579. [2] Kon and Linstead, *loc. cit.*; Kon, J., 1930, 1616. [3] Goldberg and Linstead, J., 1928, 2343. [4] Dickins, Hugh, and Kon, J., 1929, 572; Kon, *loc. cit.* [5] Kon and May, J., 1927, 1549; Hugh, Kon, and Mitchell, J., 1929, 1435. [6] Kon and Thakur, J., 1930, 2217. [7] Private communication from Dr. G. A. R. Kon, Dr. R. P. Linstead, and Mr. G. W. G. Maclennan.

The considerable difference in the mobilities of the acids of the *trans*-β-decalin and the *cyclo*hexane series can be understood when the general retarding effect of substitution in the latter (last three columns) and the sparing solubility of the potassium salts of the former are taken into consideration. The mobilities of the esters and ketones are of the same order; the equilibrium values also are in good agreement. These results, combined with those obtained from the study of α-substitution (see Part II; following paper), seem to show that so far as the tautomeric changes are concerned the *trans*-β-decalin ring simulates the *cyclo*hexane ring and vice versa—a resemblance brought into greater relief on comparing these results with those for the other ring systems.

It would be expected that the polar, conjugational, and steric factors (Linstead, J., 1929, 2498) would operate to the same extent in both the ring compounds; but the question of strain is less certain in view of the conflicting evidence for the configuration of the *cyclo*hexane ring.

However, general considerations lead to the view that the isomeride associated with minimum strain should be favoured (Linstead, *loc. cit.*), but as the behaviour of 3- and 4-membered rings, which are assumed to be strained, has not been investigated, much stress cannot be laid on this factor.

From the present results, the utmost that can be inferred is that either the strain factor operates with equal force in both the *cyclo*hexane and the *trans*-β-decalin ring or it plays no major part in determining the mobility and equilibrium in a tautomeric system. Whichever view be adopted, it would seem that the suggestion—that a ring tends to acquire a double bond in order to relieve its strain—tentatively made by Kon and Speight to explain certain anomalies (*loc. cit.*) may require revision.

EXPERIMENTAL.

(A) *Acids.*

trans-β-Decalone (I) was prepared from *trans*-β-decalol (Rao, J., 1929, 1961; Kandiah, J., 1931, 922), isolated (86% yield) by means of light petroleum (b. p. 40—60°), and regenerated from the bisulphite compound, which had been washed with Et_2O to remove the unoxidised decalol (13%). The ketone had b. p. 127—128°/23 mm. (semicarbazone, m. p. 192—193°), $d_{4°}^{22·1°}$ 0·97663, $n_D^{22·1°}$ 1·4827, $[R_L]_D$ 44·46 (calc., 44·11).

Condensation of trans-*β-Decalone with Ethyl Bromoacetate. Preparation of Ethyl* 2-*Hydroxy*-trans-*decalin*-2-*acetates* (II, III).—The yield of hydroxy-ester obtained in the Reformatsky reaction (compare Rao, J., 1930, 1182) varied from 35 to 79% (67% on the average) according to the purity of the ethyl bromoacetate. The product, b. p. 140—150°/1 mm., gave two fractions, (1) $d_{4°}^{23·5°}$ 1·01636, $n_D^{23·5°}$ 1·4798, whence $[R_L]_D$ 66·7 (calc., 65·73), (2) $d_{4°}^{23°}$ 1·0333, $n_D^{23°}$ 1·47907, whence $[R_L]_D$ 65·92, and left a residue. This was hydrolysed with cold 10% methyl-alcoholic NaOH, and the neutral part obtained as a solid which, after several crystns. from MeOH or light petroleum (b. p. 60—80°), gave $\Delta^{2\ (\text{or}\ 1)}$-trans-*octahydronaphthyl*-2-trans-*β-decalone* in colourless crystals, m. p. 125—126° (Found: C, 83·7; H, 10·4. $C_{20}H_{30}O$ requires C, 83·8; H, 10·6%). The *semicarbazone* crystallised from C_6H_6 in spindle-like clusters of needles, m. p. 209—210° (decomp.) (Found: C, 73·6; H, 9·7; N, 12·1. $C_{21}H_{33}ON_3$ requires C, 73·4; H, 9·7; N, 12·2%). The *oxime* had an indefinite m. p. and by crystn. from C_6H_6 two fractions were obtained, m. p. 180—190° and 198—203° (decomp.) (Found: C, 79·7; H, 10·4. $C_{20}H_{31}ON$ requires C, 79·7; H, 10·3%).

Hydrolysis of the Hydroxy-ester: 2-Hydroxy-trans-*decalin*·2-*acetic Acids* (IV, V, VI).—The hydroxy-ester was treated with cold 10% methyl-alcoholic NaOH for 24 hrs.; acidification then produced a hard solid (contrast Rao, *loc. cit.*).

Acid A. The crude hydroxy-acid was thrice boiled with H_2O and the first two filtrates were rejected. The third deposited crystals (recryst. from C_6H_6–petroleum, clusters of rectangular plates, m. p. 115—116°), which were removed while still warm; the mother-liquor, on cooling, deposited needles, m. p. 125—131°, which on further crystns. from C_6H_6–petroleum gave stellate clusters of prisms, m. p. 139—140° (Found: C, 67·7; H, 9·3. $C_{12}H_{20}O_3$ requires C, 67·9; H, 9·5%). When the crude hydroxy-acid was boiled three times with dil. EtOH, and the residual acid crystallised from C_6H_6, it melted at 100—133°. On progressive crystn. from C_6H_6, gritty cubic crystals, m. p. 140—141° after sintering, of the *acid A* (IV) were finally obtained.

Acid B. After a few crystns. from C_6H_6, the *2-hydroxy*-trans-*decalin-2-acetic acid* (V) had m. p. 116—118° (Rao gives m. p. 102°) (Found : C, 67·6; H, 9·4; equiv., by titration, 211·8. $C_{12}H_{20}O_3$ requires C, 67·9; H, 9·5%; equiv., 212·2). The same acid was obtained in the pure state by the hydrolysis of the residue remaining after distillation of the hydroxy-ester.

Acid C. The first C_6H_6 mother-liquor obtained above was evaporated, and the residue crystallised twice from light petroleum (b. p. 40—60°). This gave the *acid C* (VI), m. p. 90—91° (Found : C, 67·6; H, 9·5%; equiv., by titration, 212·6). This acid could also be obtained by refluxing the crude hydroxy-acid with light petroleum (b. p. 40—60°) and cooling the filtrate in ice. The residue, on evaporation of the solvent from the mother-liquor, crystallised from petroleum (b. p. 60—80°) in stellate clusters of prisms, m. p. 88°.

Dehydration of the Hydroxy-acid: trans-*Decahydronaphthylidene-2-acetic Acids* (VII, VIII).—The crude hydroxy-acid (60 g.) was boiled under reflux with Ac_2O (80 c.c.) for 2½ hrs., and the unsaturated acids were isolated by Rao's procedure (*loc. cit.*). The yield was very good but the solid acid was accompanied by varying amounts of a viscous liquid.

Partial esterification. The crude acid (315 g.), *N*-alc. HCl (250 c.c.), and abs. EtOH (625 c.c.) were left together at room temp. for 46 hrs. in order to ensure that all the $\beta\gamma$-acid was esterified. 195 G. of solid acid were recovered and the ester (107 g., b. p. 127—143°/1 mm.) gave on fractionation the $\beta\gamma$-ester (82 g., b. p. 121°/1 mm.), a mixture of the $\alpha\beta$- and the $\beta\gamma$-ester (10 g.), and a mixture probably of the $\alpha\beta$- and the hydroxy-esters (15 g., b. p. 133°/1 mm.).

$\alpha\beta$-Acid A. The sparingly sol. acid A (VII) (m. p. 135°) separated on crystn. of the above unesterified acid from *n*-hexane–light petroleum (b. p. 40—60°). Recryst. from light petroleum (b. p. 60—80°), it gave colourless needles, m. p. 143° (Rao, m. p. 145°). It had an iodine addition of 0·4% (10 mins.).

The *dibromide* (XVI) was prepared from the $\alpha\beta$-acid (3·5 g.) and Br (3 g.) in dry $CHCl_3$. After 24 hrs., the solvent was removed under reduced pressure, and the residual solid boiled with a little light petroleum (b. p. 60—80°) and crystallised from C_6H_6; small stout rhombic crystals, m. p. 155° (Rao gives m. p. 170°) (Found: C, 40·7; H, 5·1. $C_{12}H_{18}O_2Br_2$ requires C, 40·7; H, 5·1%). The determination of the equivalents of this and other dibromo-acids with $Ba(OH)_2$ was not successful.

The *amide* (XIII) was prepared by passing dry NH_3 into an ethereal solution of the undistilled $\alpha\beta$-acid chloride—formed from 1 g. of the $\alpha\beta$-acid and 0·6 c.c. of thionyl chloride, the excess of the latter being removed under reduced pressure below 40°—cooled in ice. After filtration and washing with hot H_2O, it had m. p. 180—184° and crystallised from C_6H_6 in plates, m. p. 187—188° (with previous shrinking) (Found: C, 74·5; H, 9·8. $C_{12}H_{19}ON$ requires C, 74·6; H, 9·9%). It depressed the m. p. of the $\beta\gamma$-amide (XV) considerably. When the distilled $\alpha\beta$-acid chloride was used in the preparation, the amide obtained melted at 142—143° after crystn. from C_6H_6 and four further crystns. were necessary to get the substance of m. p. 185—186°.

$\alpha\beta$-Acid B (VIII). On concentration of the hexane–petroleum mother-liquor, a colourless *acid*, m. p. 85°, separated; m. p. 95—96° after further crystn. from hexane (Found: C, 74·1; H, 9·1; equiv., by titration, 193·9.

$C_{12}H_{18}O_2$ requires C, 74·2; H, 9·3%; equiv., 194·2). It had an iodine addition of 0%. It was very soluble in light petroleum (b. p. 60—80°) and slowly crystallised from it in clusters of radiating prisms.

The ester (XI), obtained through the Ag salt, was treated with ozonised oxygen in $CHCl_3$ at 0°. *trans*-β-Decalone (b. p. 113—114°/13 mm.) was isolated by steam-distillation and extraction with Et_2O and identified by its characteristic smell and semicarbazone (m. p. and mixed m. p. 192—193°).

The *dibromide* (XIII) was prepared from the αβ-acid B (3 g., m. p. 80°) as described on p. 2129. The sticky mass left after removal of the solvent was boiled with petroleum (b. p. 60—80°); the undissolved solid crystallised from C_6H_6–petroleum (b. p. 60—80°) in needles, m. p. 143—144° (Found : C, 40·9; H, 5·1. $C_{12}H_{18}O_2Br_2$ requires C, 40·7; H, 5·1%). It depressed the m. p. (155°) of the dibromide A to 135° (decomp.).

An ethereal solution of the *amide* (XIV), prepared from the undistilled acid chloride of (VIII) as described on p. 2129, was filtered; the bulk of the solid compound, after being washed with hot H_2O, melted at 146—165°. On crystn. from C_6H_6, a small amount of sparingly soluble, silky plates, m. p. 187—188°, was obtained; the filtrate on evaporation left a residue, m. p. 145—147° after recrystn. from C_6H_6 (Found : C, 74·7; H, 9·9. $C_{12}H_{19}ON$ requires C, 74·6; H, 9·9%). The ethereal solution contained a solid which crystallised from C_6H_6 in plates, m. p. 145—147°. When the amide was formed from distilled acid chloride, it melted at 134—135° after crystallising from C_6H_6. After several crystns., some αβ-amide (XIII), m. p. 185—186°, was isolated, the rest being a very low-melting mixture.

In the dehydration experiments, if the Ac_2O was removed in a vac. at 50—60° without addition of H_2O so that the operation took 8 hrs., the yield of the acid product was considerably reduced. After treatment of the neutral oil with hot alkali for a long time, no appreciable quantity of acid was obtained on acidification. This neutral portion, on distillation under reduced pressure, gave a few drops of Ac_2O and then a thick liquid which partly solidified; after filtration, a colourless solid, m. p. 99° after crystn. from petroleum (b. p. 60—80°), was obtained and identified as the βγ-acid (IX). After the oily filtrate had been heated with dil. Na_2CO_3 aq. for some hrs., the alkaline liquid gave the βγ-acid, m. p. 99°, on acidification. The residual neutral oil had a turpentine-like odour and boiled at 81—83°/9 mm. It was redistilled and then had $d_{4°}^{16°}$ 0·8928, $n_D^{16°}$ 1·4870, whence $[R_L]_D$ 48·37 (calc., 48·13). It gave *trans*-β-decalone on oxidation with 3% $KMnO_4$ aq. and was *2-methylene-*trans*-decalin* (XIX) (Found : C, 87·7; H, 11·9. $C_{11}H_{18}$ requires C, 87·9; H, 12·1%).

A current of NOCl was passed into a $CHCl_3$ solution of the hydrocarbon at 0°. The nitrosochloride, obtained as a thick green liquid by evapn. of the solvent in vac., was heated with an alc. solution of piperidine for some mins. on the steam-bath. On cooling and partial evaporation of the solvent, colourless crystals separated; these were washed with ice-cold MeOH and fractionally crystallised from this solvent. The sparingly sol. *nitrolpiperidide A* (XX) formed rhombic silky plates, m. p. 197—198° (decomp.), from $CHCl_3$–Me_2CO (Found : C, 72·5; H, 10·6. $C_{16}H_{28}ON_2$ requires C, 72·7; H, 10·7%). The more sol. *nitrolpiperidide B* (XXI) formed very minute, gritty, prismatic crystals, m. p. 153—154° (Found : C, 72·7; H, 10·6%). Mixed m. p. of the two, 145—180°.

The αβ-acid (8 g.) was heated with pyridine (3 g.) and Ac_2O (3 g.) on the steam-bath and then at 130° for a few hrs. The product, after removal of pyridine by washing, was treated with hot alkali, which extracted very little acid. The neutral portion distilled (b. p. 186°/11 mm.) to a viscous liquid, which solidified and was crystallised from petroleum (b. p. 60—80°) and identified as the βγ-acid.

Dehydration of the Hydroxy-ester.—(i) *With phosphorus oxychloride.* The hydroxy-ester (160 g.), $POCl_3$ (60 g.), and C_6H_6 (450 c.c.) were refluxed for some hrs. The unsaturated ester (128 g.; 81% yield) had b. p. 149—152°/8 mm., $d_{4°}^{20·9°}$ 0·9964, $n_D^{20·9°}$ 1·4862, $[R_L]_D$ 64·04 (calc., 63·82), and J 46·7% (10 mins.) and 59·4% (30 mins.). (ii) *With thionyl chloride* (Darzens, *Compt. rend.*, 1911, **152**, 1601). To a solution of the hydroxy-ester (190 g.) in pyridine (125 g.), cooled in ice, were added thionyl chloride (100 g.), drop by drop, and then, after 3 hrs., ice and H_2O. The whole was heated on the steam-bath, and the ethereal solution washed with dil. HCl aq., very dil. NaOH aq., and H_2O and dried. The ester (168 g.; 95% yield) boiled at 158—162°/12 mm.

Each of the above esters on hydrolysis with cold 10% aq.-alc. NaOH yielded a solid acid with adhering liquid. The βγ-acid (purified by partial esterification) crystallised from light petroleum (b. p. 60—80°) in colourless rhombic plates, m. p. 99—100° (Rao gives 100—101°), and J 75%. Its dibromide, cryst. from C_6H_6–petroleum (b. p. 60—80°), had m. p. 181° (Rao, m. p. 183°). The *amide*, prepared from the distilled acid chloride and NH_3 in cooled Et_2O was not very sol. in C_6H_6, $CHCl_3$, AcOEt, or Me_2CO and crystallised from C_6H_6 in feathery crystals and from Me_2CO in radiating rectangular prisms, m. p. 181—182° (Found: C, 74·3; H, 9·7. $C_{12}H_{19}ON$ requires C, 74·6; H, 9·9%).

Oxidation. The pure βγ-ester (10 g.) was ozonised in $CHCl_3$ at 0°, and the product decomposed and steam-distilled. The distillate, extracted in Et_2O, had a pleasant odour and gave a red coloration with $FeCl_3$ and a violet coloration with Schiff's reagent. The non-volatile residue was treated with alkali, and the neutral portion extracted with Et_2O. The acid obtained from the alkaline liquid was extracted with much Et_2O, leaving a viscous liquid which partly solidified. After filtration the colourless crystalline solid was identified as *trans-cyclo*hexane-1 : 2-diacetic acid: the liquid portion (which gave only a very small quantity of a semicarbazone, m. p. 195°, after a long time) was oxidised with cold 3% $KMnO_4$ aq. to the same acid, m. p. (after crystn. from very dil. EtOH or H_2O) and mixed m. p. 167°. This acid could be obtained more readily by oxidising the liquid acid with hot dil. HNO_3. The liquid portion, from the above acid, gave a good amount of the *semicarbazone* of *trans-cyclo*hexane-2-acetone-1-acetic acid, very small, rhombic plates, m. p. 195—196° (decomp.), from much abs. EtOH, sparingly sol. in C_6H_6 and $CHCl_3$ (Found: C, 56·3; H, 8·2; N, 15·7, 16·1.* $C_{12}H_{21}O_3N_3$ requires C, 56·5; H, 8·2; N, 16·5%).

In another ozonisation experiment the acid from the alkaline layer gave *trans-cyclo*hexane-1 : 2-diacetic acid without further oxidation, and the filtrate readily yielded a *semicarbazone*, m. p. 164°, of *trans-cyclo*hexane-2-γ-carbethoxyacetone-1-acetic acid (Found: C, 55·0, 54·8 *; H, 7·9, 7·8 *; N, 12·9, 13·0.* $C_{15}H_{25}O_5N_3$ requires C, 55·0; H, 7·7; N, 12·9%). Unlike the semicarbazone, m. p. 196°, it did not dissolve even in hot EtOH, H_2O, or other solvents.

Iodine Additions, J.—To overcome the difficulty of dissolving the αβ-acid

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* Analyses marked * were made by Dr. Ing. A. Schoeller.

(*M*/300) in sat. $NaHCO_3$ aq. (50 c.c.) and that arising from the separation of the sodium salts therefrom on cooling, 5 c.c. of 10% Na_2CO_3 aq. were used to dissolve the acids (*M*/300) and the solution was made up with H_2O. Variation in the amount of the alkaline solution did not affect the results, the iodine additions of the *αβ*- and the *βγ*-acid being respectively identical when either 5 c.c. or 10 c.c. of the Na_2CO_3 solution were used to dissolve the acids (*M*/300). In the whole course of the work, however, 5 c.c. of the 10% solution was adopted as standard.

As the values of *J* for the *βγ*-acid were found to vary with temp. and other experimental conditions, the iodometric analyses were carried out in a dark room at approx. constant temp. In order to avoid the " back reaction " after the addition of H_2O, the whole was shaken with 20 c.c. of $CHCl_3$, then acidified with 10% HCl aq. (10 c.c.), and titrated with $Na_2S_2O_3$ (Linstead and May, J., 1927, 2565).

Reference curve.

Mixture (% *αβ* A) ...	0	10	25	50	60	75	90	100
J, %	74·1	69·3	61·1	43·4	35·6	23	9·9	0·5

Test mixtures .... 40% *αβ* : Found, 51·3; calc., 51.
20% *αβ* : Found, 63·7; calc., 63·9.

Mixture (% *αβ* B)	0	10	15	20	100
J, %	74·3	68·9	67·8	63·9	0

Equilibrations. The results of equilibrating the *αβ*- and the *βγ*-acid with KOH aq. are in Table II. The molecular weights (*M*) of the products were determined by titration with *N*/10-baryta.

TABLE II.

Acid.	KOH, %.	Temp.	Time, hrs.	*M*.	*J*, %.	Comp., % *αβ*.
αβ A	† [10] × 25	100°	50	—	12	87·5
,,	[10] × 20	,,	50	—	23·8	74
,,	,,	,,	120	—	41·7	52·5
,,	,,	,,	200	—	53·7	36·5
,,	,,	,,	340	—	61·7	24
,,	[10] × 25	B. p.	48	194·5	55·4	34
,,	,,	,,	72	194·7	63·5	21
,,	[10] × 20	,,	168	194·6	67·9	12
,,	[15] × 20	,,	264	194·8	67·4	13, 13 *
αβ B	,,	,,	168	—	65·6	16·5, 17 *
βγ	[10] × 25	100	48	—	69·8	8
,,	[10] × 20	B. p.	168	193·8	67·8	12
,,	[15] × 20	,,	168	—	67·8	12
,,	,,	,,	264	194	68·4	11, 12 *
,,	[20] × 25	,,	72	194·4	68·3	11

* These results were obtained, as a check, by determining the composition of a mixture (50 : 50) of the equilibrated acid and the pure *αβ*-acid (compare Kon and Thakur, *loc. cit.*).

† The figures in brackets show how many multiples were taken of the theo. quantity of KOH aq. required to neutralise the acid used in the expt.

The value of the equilibrium point is thus 12 ± 1% *αβ* (compare Rao, *loc. cit.*); that of the mobility is given on p. 2125.

Partial Esterification of the Equilibrated αβ-Acid B.—The acid (3·75 g.) was partially esterified for 14 hrs. The unesterified acid (0·63 g.; 17%) was crystallised from light petroleum (b. p. 60—80°), in which it was less sol. than either the *βγ*-acid or the *αβ*-acid B; m. p. and mixed m. p. with *αβ*-acid A, 140—142°. The ester (b. p. 146°/6 mm., $n_D^{20°}$ 1·48327) on hydrolysis gave an acid (1·77 g.; 72%) which was identified as the βγ-acid, m. p. and mixed m. p. 98°.

Action of Ultra-violet Light.—(i) A $CHCl_3$ solution of the αβ-acid A (2 g.) was exposed to the light for 10 days. The resulting acid had *J* 13·5%, corresponding to 14% βγ-acid, but attempts to isolate the latter by fractional crystallisation failed, the original acid, m. p. 139—141°, being obtained.

(ii) The αβ-acid B (4 g.) when similarly treated for 250 hrs. had an iodine addition of 15·8%, corresponding to 17% βγ-acid. When crystallised from petroleum (b. p. 60—80°), it gave one large tuft of crystals, m. p. 135—142°, on long standing. The acid from the hydrolysis of the ester obtained by partial esterification did not solidify even after a long time.

(B) *Esters.*

Esterification of the αβ-Acid A (VII). *Ethyl* trans-*Decahydronaphthylidene-2-acetate A* (X).—(i) *Through the silver salt.* The acid dissolved with difficulty in hot dil. NH_3 aq. The ester was washed once with very dil. NaOH aq. to remove any αβ-acid; otherwise this acid distilled with the ester and separated in a cryst. form. The *ester* had b. p. 160°/7 mm.; $d_{4°}^{20°}$ 0·99883, $n_D^{20°}$ 1·49983, whence $[R_L]_D$ 65·4 (calc., 63·82); *J* 1·3% (30 mins.) and 2·3% (60 mins.) (Found: C, 75·3; H, 9·9. $C_{14}H_{22}O$ requires C, 75·6; H, 10·0%).

(ii) *By alcoholic hydrogen chloride* (Kon and Linstead, *loc. cit.*). The αβ-acid (12 g., m. p. 140°), abs. EtOH (25 c.c.), and *N*-alc. HCl (15 c.c.) were heated together on the steam-bath for 3 hrs. and left over-night at room temp.; about 1 g. of the acid was recovered. The ester (11·5 g.) had b. p. 167°/13 mm., $d_{4°}^{20°}$ 0·9988, $n_D^{20°}$ 1·49944 (whence $[R_L]_D$ 65·36), and *J* 3·3% (60 mins.).

Esterification of the αβ-Acid B (VIII).—(i) *Through the silver salt.* The acid dissolved readily in dil. NH_3 aq. *Ethyl* trans-*decahydronaphthylidene-2-acetate B* (XI) was distilled without preliminary washing with aq. alkali and had b. p. 160°/9 mm.; $d_{4°}^{20°}$ 0·99874, $n_D^{20°}$ 1·49964, whence $[R_L]_D$ 65·39 (calc., 63·82); *J* 1·3% (10 mins.) and 1·9% (30 mins.) (Found: C, 75·3; H, 9·8%).

(ii) *By alcoholic hydrogen chloride.* This was done as in the case of the αβ-acid A, and the ester obtained had *J* 3·2% (60 mins.).

The acid obtained on hydrolysis of the above ester (2 g.) was a viscous mass, which solidified and then crystallised from light petroleum (b. p. 60—80°) in prismatic needles, m. p. 95—96° (depression with the βγ-acid, m. p. 99°).

Esterification of the βγ-Acid (IX).—(i) *Through the silver salt.* The acid dissolved readily in dil. NH_3 aq. *Ethyl* Δ^2-trans-*octahydronaphthalene-2-acetate* (XII; formula as IX) had b. p. 153—154°/9 mm.; $d_{4°}^{19·2°}$ 0·99346, $n_D^{19·2°}$ 1·48365, whence $[R_L]_D$ 63·94 (calc., 63·82); *J* 66·3% (30 mins.) and 76·5% (60 mins.) (Found: C, 75·4; H, 9·8%).

(ii) *By alcoholic hydrogen chloride.* The βγ-acid was left with alc. HCl for 10 hrs. at room temp., the quantities used for partial esterifications (Kon and Thakur, *loc. cit.*) being taken. The ester had b. p. 164—165°/18 mm., $d_{4°}^{20°}$ 0·99344, $n_D^{20°}$ 1·48337 (whence $[R_L]_D$ 63·91), and *J* 76·4% (60 mins.).

Reference curve. The values of *J* refer to the % iodine additions in 60 mins. under the conditions of Linstead and May (*loc. cit.*).

% αβ	0	10	20	40	50	60	80	90	100
J, %	76·5	72·8	67·6	55·5	47·9	39·8	22	12	2·3

The αβ-ester A was used in the above mixtures. The values obtained by using the αβ-ester B were the same and are not recorded. Hence the same reference curve served for the two isomerides.

Action of Sodium Ethoxide on the Esters.—Abs. EtOH dried over Ca was used. The esters were treated with NaOEt under Kon and Linstead's standard conditions (unless otherwise stated). The method of isolating the ester was the same as Kon and Linstead's (*loc. cit.*, p. 1278) except that the NaOEt solution of the ester was pipetted into H_2O instead of into $N/2$-H_2SO_4 (3 v. c.c.); consequently, it was not necessary to wash with alkali and the aqueous layer gave the acid on acidification. For the iodometric analysis, the latter was purified by means of Na_2CO_3 aq.

The b. p.'s of the equilibrated esters never exceeded that of the pure αβ-ester and no direct evidence of the formation of ethoxy-ester to any appreciable extent was obtained. From the various experiments, the residues left after

TABLE III.

		Acid Product.		Unsaturated Ester.					
Expt.	Time, hrs.	% Re-covered.	Comp., % βγ.	% Re-covered.	$d^{t°}_{4°}$.	$n^{t°}_{D}$.	J, %.		Comp., % αβ.
1	6				0·9965/20°	1·4961	15·5	86	
2	15			88	0·9965/20	1·4923	28·1	73	
3	25				0·9961/20·1	1·4904	36·7	64	
4	39				0·9968/20·2	1·4892	45·6	53	
5	50				0·9961/20·3	1·4886	48·5	49	
6	62				0·9961/19·9	1·4885	50·2	47	
7	75				0·9952/20·5	1·4881	53·3	42·5	
8	120	5·5		82	0·9954/20·1	1·4881	55·4	40	
9	240				0·9955/20	1·4880	52·8	43·5	
10	360				0·9953/20	1·4880	53·7	42	
11	252	10·3	86	i 59	0·9954/20	1·4876	55	40·5	41*
				ii 25	0·9961/20	1·4879	44	55	
12	337	15·2	89	67	0·9955/20	1·4880	50·9	46	40*
13	164	45	89·5	41	0·9945	1·4897	38·9	61	36*
14	5	8·7	86·5	80	0·9947/20	1·4868	59·8	34	
15	27	27·7	88·5	—	0·9945/20	1·4868	58·7	36	
1	12			86·6	0·9974/20·2	1·4947	17·1	84·5	
2	38				0·9971/20·2	1·4899	36·1	64	
3	60				0·9957/20	1·4897	43	56	
4	90				0·9948/20	1·4887	48	50	
5	75	5		84	0·9965/20	1·4890	45·7	52·5	
6	120				0·9954/20·2	1·4885	51·3	45·5	
7	360	10·9	86	79·5	0·9951/20	1·4880	53·7	42	38*
1	12			80	0·9938/20	1·4852	70·2	15·5	
2	24			79	0·9942/20·1	1·4859	66·3	23	
3	50			80	0·995/19·8	1·4875	60·7	32	
4	75	2·3		83	0·9947/20	1·4875	58·7	35	
5	90			82	0·9956/20	1·4879	56·7	38	
6	120	4·6		85	0·9954/20	1·4879	55·2	40	
7	240	16·3		80	0·9955/20·1	1·4881	53·4	43	
8	360	8·1		85	0·9955/20	1·4880	53·3	43	
9†	100	12·7	89·5	78	0·9952/	1·4888	54·5	41	
10†	360	35	89	56	0·9955/20	1·4887	42·4	57	38*
11	120	7·7		85	0·9954/20	1·4880	53·7	42	

* Calc. value of equilibrium, taking the acid product into consideration.

† An excess of $2N$-NaOEt was used.

distillation of the esters were accumulated and distilled; the product had $d_{4^\circ}^{20^\circ}$ 0·9976, $n_{D}^{20^\circ}$ 1·48927, and J 28·2%, corresponding to 73% $\alpha\beta$ (Found: C, 75·4; H, 10·1. $C_{14}H_{22}O_2$ requires C, 75·6; H, 9·9%. The ethoxy-ester, $C_{16}H_{28}O_3$, requires C, 71·7; H, 10·5%).

The results of equilibrations of the $\alpha\beta$-ester A are in Table III (top portion). In Expts. 11—15 a large excess of N-NaOEt was used. Expts. 14—15 were carried out on the steam-bath, the $\alpha\beta$-ester (164 hrs.) and $\beta\gamma$-ester (100 hrs.) being used in (15). In Expt. 11, the ester was collected in two fractions.

The value of the mobility $10^4 \times (k_1 + k_2)$ for this ester is 6·9, and the half-change period, 17·5 hrs., from the mobility curve is in close agreement with the calc. value for $t_{1/2}$. For the $\alpha\beta$-ester (252 hrs. i) (Found: C, 75·3; H, 9·7. $C_{14}H_{22}O_2$ requires C, 75·6; H, 9·9%).

Table III (middle portion) summarises the results of experiments on the $\alpha\beta$-ester B.

The amount of hydrolysis was very small, considering that only 1·9 g. of acid (5·3%) were collected from all the experiments (41·5 g. of ester). The mobility calculated from these figures is 3·9, whereas the half-change period from the mobility curve, as well as that calculated, is about 27 hrs.

The results of equilibrations of the $\beta\gamma$-ester are in Table III (bottom portion).

In Expt. 11 a mixture of 50·4% of the $\alpha\beta$- and 49·6% of the $\beta\gamma$-ester was used with excess of N-NaOEt. The mobility calculated from these figures is 6 and the half-change period from the mobility curve is 20 hrs., whereas from the expression $t_{\frac{1}{2}} = \frac{1}{k_1 + k_2}\log_e 2$ it is 20·2 hrs. (Found for the equilibrated ester in Expt. 10: C, 75·6; H, 9·7. $C_{14}H_{22}O_2$ requires C, 75·6; H, 9·9%).

The value of equilibrium from all the esters may be taken as 40% $\alpha\beta$ (see Table III).

(C) *Ketones.*

Semicarbazone of trans-*Decahydronaphthylidene-2-acetone.*—(i) *From the $\alpha\beta$-acid, m. p.* 143°. The acid (20 g.) was converted by thionyl chloride (10 c.c.) into the acid chloride (21 g., b. p. 154—155°/8 mm.), which was mixed with ZnMeI in toluene in a freezing mixture (Blaise and Maire, *Ann. Chim. Phys.*, 1908, **15**, 556; Dickins, Hugh, and Kon, J., 1928, 1630). In these reactions it is preferable to wash the ether–toluene extract with very dil. NaOH aq. to remove all the $\alpha\beta$-acid, since this is only partly eliminated when Na_2CO_3 aq. is used (compare Eccott and Linstead, *loc. cit.*; Wechsler, *Monatsh.*, 1893, **14**, 462). The *semicarbazone* prepared from the ketonic distillate (17 g., b. p. 146—148°/11 mm.) was washed with light petroleum and H_2O and crystallised from C_6H_6 and Me_2CO; prismatic needles, m. p. 186° (Found: C, 67·1; H, 9·2. $C_{14}H_{23}ON_3$ requires C, 67·4; H, 9·3%).

A small amount of a very sparingly sol. semicarbazone was also obtained, m. p. 199° after crystn. from toluene. Mixed m. p. of the two semicarbazones, 187—192°.

The alkaline washing in the above reaction yielded a mixture of $\alpha\beta$ (m. p. 140°) and $\beta\gamma$ (95—96°) acids. That part of the distillate which did not react with semicarbazide acetate gave on hydrolysis the acid (m. p. 142—143°) and therefore consisted of the $\alpha\beta$-ester (compare Kon and Narayanan, *loc. cit.*).

In some of the experiments, the semicarbazone came down as a caseous mass, very sol. in Et_2O, MeOH, Me_2CO, and $CHCl_3$, but insol. in light petroleum.

It melted at 96—98° after crystallising from C_6H_6–petroleum (b. p. 60—80°) (Found : C, 67·0; H, 9·4%), but at 88—90° when light petroleum alone was used. Even those semicarbazones which had such an indefinite m. p. as 80—150° showed a tendency to form a low-melting eutectic mixture and on crystn. from C_6H_6–petroleum yielded clusters, m. p. 80—85°.

(ii) *From the αβ-acid B.* The acid chloride (20 g. from 20 g. of the acid, m. p. 85°) was a colourless mobile liquid, b. p. 152—154°/6—7 mm. This (17 g.) gave an 85% yield of a ketonic fraction, b. p. 143—145°/10 mm., with ZnMeI. The semicarbazone crystallised from C_6H_6 in fine needles, m. p. 186—187°, and from MeOH in rhombic plates. It did not depress the m. p. of the other semicarbazone (186—187°) from (i). The pure semicarbazone, unlike the low-melting eutectics, is sparingly sol. in all solvents.

In another experiment, however, the crude ketone gave a colourless crystalline semicarbazone, m. p. 131—133° without any purification. After crystn. from C_6H_6 it melted at 134—135° and was identified as the semicarbazone of Δ^2-*trans*-octahydronaphthyl-2-acetone.

(iii) *From the hydroxy-acid, m. p.* 116—118° (compare Kon and Narayanan, J., 1927, 1546). The hydroxy-acid (20 g.) on treatment with thionyl chloride (20 c.c.) gave an acid chloride (10 g., b. p. 150—154°/9 mm.). The ketone (5 g., b. p. 152°/17 mm.) gave a semicarbazone which after several crystns. from C_6H_6–light petroleum melted at 185—186° and was identical with that obtained from the αβ-acids A and B. The more soluble fraction, to which the crude semicarbazone owed its indefinite m. p., was the βγ-semicarbazone. The acid, m. p. 94—95°, recovered from the alkaline washing was the βγ-acid.

The same intractable mixture of semicarbazones was obtained when MgMeI or $ZnMe_2$ was used instead of ZnMeI in the synthesis of the αβ-ketone from the αβ-acid chlorides A and B.

Semicarbazone of Δ^2-trans-*Octahydronaphthyl*-2-*acetone*.—The βγ-acid (m. p. 97°) (20 g.) and thionyl chloride (10 c.c.) yielded a colourless acid chloride (19 g., b. p. 145—146°/11 mm.). The ketone (12 g., b. p. 143—145°/10 mm.) prepared from it by the Blaise–Maire reaction gave a *semicarbazone*, needles or very thin plates, m. p. 135°, from C_6H_6–light petroleum (b. p. 60—80°) (Found : C, 67·5; H, 9·2. $C_{14}H_{23}ON_3$ requires C, 67·4; H, 9·3%). The βγ-acid, m. p. 96—97°, was obtained from the alkaline washing.

Preparation of trans-*Decahydronaphthylidene*-2-*acetone from its Semicarbazone*.—The semicarbazone was shaken with $N/2$-H_2SO_4 and petroleum for 69 hrs. (Kon, *loc. cit.*) : only a small quantity of ketone was formed. The residue after removal of the petroleum was therefore steam-distilled with a large excess of oxalic acid. The *ketone* was extracted with Et_2O, washed with H_2O, 10% Na_2CO_3 aq., and again with H_2O and distilled. It had b. p. 149—150°/15 mm.; $d_{4^\circ}^{20\cdot3^\circ}$ 0·9734, $n_D^{20\cdot3^\circ}$ 1·5068, whence $[R_L]_D$ 58·6 (calc., 57·38); J 25·1% (10 mins.) (Found : C, 81·0; H, 10·4. $C_{13}H_{20}O$ requires C, 81·2; H, 10·5%). On oxidation with cold 3% $KMnO_4$ aq. in $NaHCO_3$ suspension it yielded decalone, identified by its characteristic odour and its semicarbazone (m. p. and mixed m. p. 193°).

Preparation of Δ^2-trans-*Octahydronaphthyl*-2-*acetone*.—Kon's method proving extremely slow, the semicarbazone was hydrolysed with oxalic acid as described above (Found: C, 80·9; H, 10·3. $C_{13}H_{20}O$ requires C, 81·2; H, 10·5%). The various preparations of the *βγ-ketone* from the semicarbazones had the following physical properties :

Semicarbazone from:	B. p.	$d_{4°}^{t°}$.	$n_D^{t°}$.	$[R_L]_D$ (calc., 57·38).	J, %.
Treatment with Al-Hg; m. p. 129°..............	146°/15 mm.	0·9666/20·3°	1·4939	57·86	82
βγ-acid; m. p. 128—129	145—146/15	0·9678/20·3	1·4939	57·8	82
αβ-acid B; m. p. 130 ...	145/15	0·9675/20·3	1·4950	57·92	81
βγ-acid; m. p. 130	130/9	0·9668/20·1	1·4937	57·83	81·1
αβ-acid; m. p. 175	138/9	0·9646/20·8	1·4940	58·1	84·8

From the first, fourth, and fifth preparations the ketone was isolated by steam distillation only.

Reference curve.

% αβ	0	10	25	40	50	60	75	90	100
J, % (10 mins.)	82·3	79·4	74·2	67·3	61·6	55·0	44·5	33·5	25·1

Equilibration with Sodium iso*Propoxide.*—The ketone (5 g.; regenerated by Kon's method from the semicarbazone, m. p. 85—130°, and having b. p. 135—139°/9 mm., $d_{4°}^{20·1°}$ 0·9672, $n_D^{20·1°}$ 1·4963, J 73·7%) was heated with sodium *iso*propoxide (50 c.c. of dry *iso*propyl alcohol and 0·8 g. of Na) on the steam-bath for 3 and for 6 hrs. The two samples boiled at nearly the same temp., 106—120°/9 mm., giving poor yields of distillate, and considerable residues were left in the distilling flasks. The distillate was a thick colourless liquid with the odour of *trans*-β-decalol; it gave no semicarbazone and after a long time deposited crystals, m. p. 75—76°, of *trans*-β-decalol.

The following experiments (Table IV) were carried out under Kon and Linstead's conditions to determine the mobility and the position of equilibrium.

TABLE IV.

Expt.	Ketone.	Time.	B. p.	$d_{4°}^{t°}$.	$n_D^{t°}$.	J, %.	Comp., % αβ.
1	βγ	5 mins.	144—146°/15	0·9668/20·7°	1·4945	78	13·5
2	,,	10 ,,	144—146/15	0·9666/20·8	1·4953	75·9	19·5
3	,,	20 ,,	144—146/15	0·9662/21	1·4962	73	27·5
4	,,	30 ,,	,,	0·9666/21·1	1·4965	69·8	34·5
5	,,	40 ,,	,,	0·9666/21·2	1·4966	69·8	34·5
6	,,	60 ,,	146—147/15	0·9686	1·4975	69·4	35·5
7	,,	3 hrs.	140—141/10	0·9689/20·1	1·4971	70·4	33·5
8	,,	2 ,,	146—147/15	0·9684	1·4974	67·7	39
9	,,	3 ,,	139/10	0·9682/20	1·4961	65·2	44
10	—	24 ,,	149—151/14	0·9646/20	1·4959	63·7	46·5
11	—	23 ,,	148—149/16	0·9659/20·2	1·4958	65	44
12	αβ	15 ,,	144—147/15	0·9700/20·3	1·4957	61	50·5

In Expts. 1—9, pure βγ-ketone was used. In Expt. 7, the ketone was regenerated from the semicarbazone, m. p. 175°. In Expt. 10, the ketone recovered from Expts. 7 and 9 was used. In Expt. 11, the ketone recovered from Expts. 1—3 was used. In Expts. 6—12, a large excess of approx. N-NaOEt was used.

The accumulated residues from the distillations in some of the above experiments had the following physical properties: b. p. 148—152°/15 mm., $d_{4°}^{20·3°}$ 0·9685, $n_D^{20°}$ 1·4948, J 63% corresponding to 47·5% αβ. The low value for the refraction is noteworthy. An attempt to isolate ethoxy-semicarbazone from the equilibrated αβ-ketone was unsuccessful on account of the difficulty of inducing the resulting semicarbazone to crystallise. The βγ-ketone, equilibrated for 1 hr., was analysed (Found: C, 80·8; H, 10·35. $C_{13}H_{20}O$ requires

C, 81·2; H, 10·5%. The ethoxy-ketone, $C_{15}H_{26}O_2$, requires C, 75·6; H, 10·9%).

The equilibrium value is 35% $\alpha\beta$ and the mobility is of the order 800. The half-change period calc. from the usual expression is 8·2 mins., which is in close agreement with that found from the mobility curve, *viz.*, 8 mins.

Condensation with Ethyl Sodiomalonate.—The ketone (9·6 g., recovered from the equilibrations) was heated with ethyl malonate (8 g.) and Na (1·2 g.) in 32 c.c. of EtOH for 8 hrs. on the steam-bath (Norris and Thorpe, *loc. cit.*). The uncondensed ketone and ester were removed and the dihydroresorcinol ester was obtained as a semi-solid on acidification of the alkaline layer. It solidified in vac. with considerable frothing, but became semi-solid again on exposure to the air. In this respect it offered a remarkable contrast to the corresponding compound of *cyclo*hexane, which was a viscous gum in vac. but solidified on exposure to the air (Norris and Thorpe, *loc. cit.*). All attempts to crystallise it were fruitless. On hydrolysis with 20% KOH aq. for 2 hrs. on the steam-bath and acidification with HCl aq. a cryst. solid was obtained. This was sparingly sol. in petroleum (b. p. 60—80°) but crystallised from AcOEt–petroleum (in rhombic plates), C_6H_6–petroleum, or $CHCl_3$. trans-*Decalin*-2-spirocyclo*hexane*-2′ : 6′-*dione* decomposed at 185° to a yellow opaque mass, clearing at 186° to a red liquid (Found : C, 76·5; H, 9·2. $C_{15}H_{22}O_2$ requires C, 76·8; H, 9·5%).

Condensation of trans-*β-Decalone with Acetone.*—A mixture of decalone (38 g.) and dry Me_2CO (15 g.) having been added portionwise to 400 c.c. of NaOEt solution (containing 5% Na) cooled in ice (Wallach, *loc. cit.*), the whole was left at 0° for some hrs. and then at room temp. for 4 days. Much H_2O was added and after ether extraction the residue was submitted to steam-distillation, 2 l. of distillate being collected : from this Et_2O extracted decalone (10 g.), b. p. 124—128°/14 mm., and the condensation product, b. p. 110—120°/1 mm. The required ketone being only slightly volatile in steam, the remainder of the residue was distilled, giving (i) a ketonic liquid (5 g.), b. p. 116—125°/1 mm., (ii) a fraction (3 g.), b. p. 160°/1 mm., which did not yield a semicarbazone, and (iii) undistilled part (15 g.). Both the ketonic fractions gave a *semicarbazone*, m. p. 96—98° after crystn. from petroleum (b. p. 60—80°) (Found : C, 67·0; H, 9·3. $C_{14}H_{23}ON_3$ requires C, 67·4; H, 9·3%). The *ketone* regenerated by steam-distillation with oxalic acid had b. p. 141°/13 mm.; $d_{4^\circ}^{20^\circ}$ 0·9693, $n_D^{20^\circ}$ 1·49405, whence $[R_L]_D$ 57·71 (calc., 57·38); J 70·8%, corresponding to 67·5% of $\beta\gamma$-ketone, *i.e.*, roughly the equilibrium mixture (Found : C, 80·9; H, 10·3. $C_{13}H_{20}O$ requires C, 81·2; H, 10·5%).

trans-β-Decalone (15·6 c.c.) and dry Me_2CO (6·4 c.c.) were refluxed on the steam-bath with magnesium butoxide for 24 hrs. (Grignard and Fluchaire, *loc. cit.*). The product was diluted with H_2O, extracted in Et_2O, and washed with dil. HCl aq. and H_2O. On distillation, decalone was recovered and a ketone (3 g., b. p. 140—150°/13 mm.) was obtained which gave an intractable semicarbazone.

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