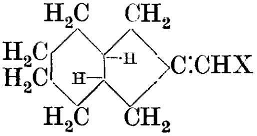
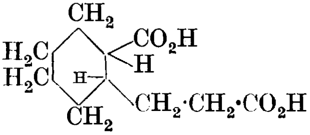
299. *Three-carbon Tautomerism in Dicyclic Systems. Part III. A Comparison between Corresponding Compounds of* trans-*Hexahydrohydrindene and* cyclo*Pentane.*

By R. S. THAKUR.

HÜCKEL and FRIEDRICH have shown that a five- and a six-membered ring can be fused together in the 1 : 2-position by their *cis*- as well as by their *trans*-valencies just like the two *cyclo*hexane rings in *cis*- and *trans*-decalins (*Annalen*, 1926, **451**, 132). Their work on hexahydrohydrindene compounds has proved beyond doubt the correctness of their view (compare also Baeyer, *Annalen*, 1890, **258**, 217; Gurney, Perkin, and Plant, J., 1927, 2676; Perkin and Plant, J., 1928, 639; Plant and Rosser, J., 1929, 186; Blount, Perkin, and Plant, *ibid.*, p. 1975). The models of the two hexahydrohydrindenes (*Annalen*, 1926, **451**, 134) show that the *cis*-fusion involves hardly any strain; on the other hand, in the *trans*-interlocking, the two *trans*-valencies taking part in the formation of the *cyclo*pentane ring deviate from their normal positions to an equal extent, the value of the deflexion being between that involved in the formation of a *cyclo*pentane and a *cyclo*butane ring, *i.e.*, between 44′ and 9° 44′. Hence it would seem that the *trans*-form is under some strain. Measurements of the heats of combustion of *cis*- and *trans*-hexahydro-2-hydrindones, although in agreement with the results found for the corresponding decalin compounds, give no useful information regarding the relative state of strain in the two rings (*cis-* and *trans*-hexahydrohydrindenes). The work of Kandiah, carried out on the basis of the Thorpe–Ingold valency deflexion hypothesis, suffers from the same limitation (J., 1931, 952); he nevertheless concludes that there is no appreciable strain in either of these two dicyclic systems.

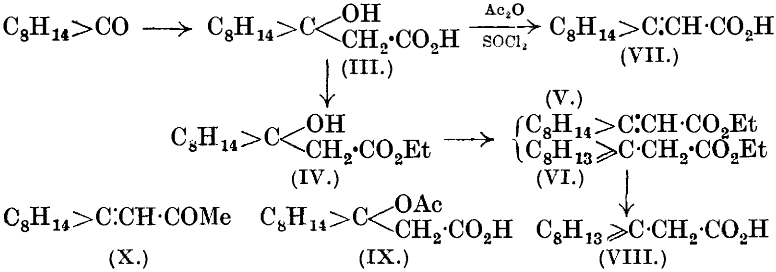
In Parts I and II of this series (preceding papers) it was shown that compounds containing the strainless *trans*-β-decalin ring closely follow the behaviour of the corresponding *cyclo*hexane compounds as regards tautomeric mobility and equilibrium. The investigation has now been extended to compounds of *trans*-hexahydrohydrindene (I): if the strain indicated on the model is reflected in the behaviour of these compounds, they should differ from the analogous *cyclo*pentane derivatives.


(I ; X = CO_2H, CO_2Et, or COMe.)


(II.)

trans-Hexahydro-2-hydrindone was prepared by the distillation of *trans-cyclo*hexane-1 : 2-diacetic acid (Kandiah, J., 1931, 936), which was obtained together with 1-carboxy-*trans-cyclo*hexane-2-propionic acid (II) by oxidation of *trans*-β-decalol with concentrated nitric acid.

The preparation of the αβ-acid, *trans*-hexahydrohydrindylidene-2-acetic acid (VII), has been described by Kandiah (J., 1931, 945). This acid is isolated in good yield in the preparation of the βγ-acid (see below). The dehydration of the hydroxy-acid with acetic anhydride was, however, repeated, but instead of the acetoxy-acid (IX) (Kandiah, *loc. cit.*), only the αβ-acid was obtained. This acid was also obtained in excellent yield when an attempt was made to prepare the acid chloride from the hydroxy-acid by treatment with thionyl chloride.



$$C_8H_{14}{>}CO \longrightarrow \underset{\text{(III.)}}{C_8H_{14}{>}C{<}^{OH}_{CH_2\cdot CO_2H}} \xrightarrow[SOCl_2]{Ac_2O} \underset{\text{(VII.)}}{C_8H_{14}{>}C{:}CH\cdot CO_2H}$$

$$\downarrow$$

$$\underset{\text{(IV.)}}{C_8H_{14}{>}C{<}^{OH}_{CH_2\cdot CO_2Et}} \longrightarrow \begin{cases} C_8H_{14}{>}C{:}CH\cdot CO_2Et & \text{(V.)} \\ C_8H_{13}{\geqslant}C\cdot CH_2\cdot CO_2Et & \text{(VI.)} \end{cases}$$

$$\downarrow$$

$$\underset{\text{(X.)}}{C_8H_{14}{>}C{:}CH\cdot COMe} \qquad \underset{\text{(IX.)}}{C_8H_{14}{>}C{<}^{OAc}_{CH_2\cdot CO_2H}} \qquad \underset{\text{(VIII.)}}{C_8H_{13}{\geqslant}C\cdot CH_2\cdot CO_2H}$$

In the esterification of the hydroxy-acid (III) with alcoholic hydrogen chloride, some dehydration occurred in the cold, and more at higher temperatures. The dehydration of the hydroxy-ester (IV) with phosphorus oxychloride, phosphoric oxide, or thionyl chloride produced a considerable proportion of the αβ-ester (V). Darzens's method (*Compt. rend.*, 1911, **152**, 1601) gave the best yield (92%) and the product contained about 42% of the βγ-ester, as shown by Linstead and May's iodometric method (J., 1927, 2565).

The unsaturated ester gave on hydrolysis a large proportion of the αβ-acid and some βγ-acid. The latter was obtained pure by partial esterification and subsequent hydrolysis. *trans*-Hexahydroindenyl-2-acetic acid was found to melt at 67°, not at 144° as stated by Kandiah (*loc. cit.*). The preparation has been repeated a number of times and it is doubtful whether Kandiah's acid, the constitution of which was not proved, could have been the pure βγ-compound. In view of the high mobility of both the acids and the esters (see below), it seems possible that the acid, m. p. 144°, was impure αβ-acid. Moreover, the βγ-acid now obtained gives a dibromide, m. p. 135° (Kandiah, m. p. 146°; compare the dibromide of the αβ-acid, m. p. 147—148°), and an *amide*, both of which considerably depress the melting points of their isomerides derived from the αβ-acid.

Some βγ-acid was also prepared—though in poor yield—by boiling the αβ-acid with aqueous potash. The pure acid, obtained by eliminating the αβ-acid by crystallisation and partial esterification, was identical with that obtained from the dehydration of the hydroxy-ester.

The conversion of the βγ- into the αβ-acid with boiling alkali and vice versa disproves the possibility of its being or containing the γδ-isomeride, which would not be expected to give the αβ-acid on equilibration (compare Goldberg and Linstead, J., 1928, 2343; also the following paper).

The pure αβ-*ester* (V) was prepared from the silver salt of the αβ-acid, whereas the βγ-*ester* (VI) was prepared by means of alcoholic hydrogen chloride.

The βγ-compounds both in this and in the *trans*-β-decalin series (preceding two papers) show appreciable exaltation of their molecular refractions. This should not be taken to indicate their containing any impurity, as it is a characteristic of all *trans*-compounds (compare Hückel, "Theoretische Grundlagen der Organische Chemie," 1931, II, 150):

Compound.	$[R_L]_D$ *cis.*	$[R_L]_D$ *trans.*	$[R_L]_D$ calc.
Decalin	43·88	44·28	43·98
β-Decalone	43·99	44·40	43·99
α-Decalone	43·90	44·24	43·99
Hexahydrohydrindene	39·31	39·62	39 36
Hexahydro-2-hydrindone	39·37	39·78	39·51

trans-Hexahydrohydrindylidene-2-acetone (X) can be readily prepared by the Blaise–Maire reaction from the αβ-acid (VII) (Kandiah, *loc. cit.*). Its αβ-structure is confirmed by the exaltation of its molecular refraction (1·79), low iodine addition, and oxidation to *trans*-hexahydro-2-hydrindone.

Various attempts were made to prepare the βγ-ketone, *trans*-hexahydroindenyl-2-acetone, but without success. (1) When the undistilled βγ-acid chloride (which gave the pure βγ-amide) was treated with methylzinc iodide, the ketonic product contained the αβ-ketone (X). That the acid chloride did not isomerise to the αβ-isomeride during the reaction is proved by the fact that pure βγ-acid was obtained from the acid chloride still remaining in the reaction product. (2) Synthesis from the hydroxy-acid (III) failed because no acid chloride could be obtained from it, as already mentioned. (3) Attempts were made to obtain it by regeneration from its sodio-derivative, prepared from the αβ-ketone (X), with benzoic acid (compare Hugh and Kon, J., 1930, 775). The yield of the ketonic product was very poor. Only a small quantity of a semicarbazone, m. p. 178—181°, was isolated, the rest consisting of a eutectic mixture, m. p. 213° (m. p. of the αβ-semicarbazone, 222°).

Tautomerism of the Acids (VII, VIII), *Esters* (V, VI), *and Ketones.*

Acids.—The potassium salts of both the αβ- and the βγ-acid do not dissolve completely in aqueous potash under Linstead's conditions (J., 1927, 2579). Despite the effect this produces on mobility (see Part I), the βγ-acid is completely equilibrated (90% change) in about four hours, and therefore these acids must be regarded as highly mobile. The order of mobility (*ca.* 6) thus found is of course only approximate and represents a lower limit. The value for the position of equilibrium is about 90% αβ. This figure is confirmed by subjecting a large quantity of the equilibrated αβ-acid to partial esterification and calculating the percentage of the βγ-acid from the quantity and composition of the ester. The latter is readily determined by Linstead and May's iodometric method (*loc. cit.*).

Esters.—The equilibrations of ethyl *trans*-hexahydrohydrindylidene- and *trans*-hexahydroindenyl-2-acetates (V and VI) were carried out under Kon and Linstead's conditions (J., 1929, 1269). The most remarkable feature is their unexpectedly high mobility; and the point of equilibrium is almost completely on the αβ-side, namely, about 98% αβ. This value is reached from the βγ-side in about five minutes. The mobility, $10^4 \times (k_1 + k_2)$ min.$^{-1}$, is greater than 5000. It is probably on account of this high mobility and the position of equilibrium on the αβ-side that a considerable proportion of the αβ-isomeride is always formed in the preparation of the βγ-ester by the dehydration of the hydroxy-ester. For the same reason, unless the hydrolysis of the βγ-ester is carried out with dilute alkali in the cold, an appreciable quantity of the αβ-acid is isolated.

Ketones.—The mobility could not be determined, as the βγ-ketone could not be synthesised. The position of equilibrium is completely on the αβ-side, since the αβ-ketone (X) undergoes no change in physical properties or iodine addition on treatment with sodium ethoxide. The methylation and ethylation of the αβ-ketone (X) are discussed in the following paper (Part IV).

The above results are tabulated in Part IV (p. 2160). It would seem from them that there are two striking characteristics of the compounds of the *trans*-hexahydrohydrindene series: (1) their very high mobility and (2) the position of equilibrium being right on the αβ-side. The only cyclic compounds which approach them in these respects are those of the *cyclo*pentane series. The likeness is not so close as that between the analogous compounds of *trans*-β-decalin and *cyclo*hexane.

The mobility of the ketones of any series is considerably higher than that of the esters of the same series on account of the greater "activating" power of the COMe in comparison with CO_2Et. Hence it must be taken that the mobility of the ketones of the hexahydrohydrindene series is unusually high.

Finally, the present study indicates that the position of equilibrium of the *cyclo*pentane acids on the βγ-side is definitely anomalous.

EXPERIMENTAL.

Oxidation of trans-*β-Decalol.*—Conc. HNO_3 (600 c.c.) was heated to its b. p. in a 3 l. flask fitted with a wide-mouthed air-condenser and, above this, a water-condenser. *trans-β*-Decalol (m. p. 75°) (200 g.) was added in small quantities: the reaction, once started, was self-maintaining. The mixture was heated for ½ hr. and kept at room temp. for 2 hrs. and the *trans-cyclo*hexane-1 : 2-diacetic acid was then washed with ice-cold water and with light petroleum (b. p. 60—80°); m. p. 164° after sintering (yield, 36—40%).

The HNO_3 mother-liquor deposited an acid (yield, 18%), m. p. 115—122° (clearing at 135°).

Oxidation of trans-*β-Decalone.*—Under Kandiah's conditions (*loc. cit.*) 330 g. of *trans-β*-decalone and 810 c.c. of conc. HNO_3 gave 195 g. (yield, 44%) of acid, m. p. 135—160°. Recrystn. from hot EtOH (300 c.c.) by addition of hot H_2O (800 c.c.) gave 140 g., m. p. 165—167°; a second crop had m. p. 120—135°, clearing at 150°.

trans-β-Decalone (95 g.) and HNO_3 (240 c.c.) gave an acid (m. p. 165—166°; 38% yield) after 2 hrs.' standing; the second crop (14%; after 18 hrs.) melted at 120—135°.

trans-*Hexahydro-2-hydrindone.*—When a mixture of *cyclo*hexane-1 : 2-diacetic acid and 7·5% of $Ba(OH)_2$ was heated (compare Kandiah, *loc. cit.*), the ketone distilled at 260—290° : more was obtained by distilling the residue under 200 mm., care being taken that the diacetic acid also did not pass over. The distillate was diluted with light petroleum (b. p. 40—60°), which effected a very good separation of the aq. layer. It was then washed with dil. NaOH aq. (from this the diacetic acid could be recovered on acidification) and with H_2O, dried with $CaCl_2$ and K_2CO_3, and distilled; b. p. 103°/21 mm. (semicarbazone, m. p. 243° without purification).

If the diacetic acid used in the preparation contained the acid (II), a mixture of *trans*-hexahydro-1- and -2-hydrindones was obtained. This was converted into the semicarbazones, which were refluxed with MeOH (800 c.c. for 80 g. of semicarbazone), the semicarbazone of the 1-isomeride passing into solution : the residual semicarbazone (m. p. 243°), steam-distilled with oxalic acid, gave *trans*-hexahydro-2-hydrindone, b. p. 103°/21 mm., $d_{4°}^{20°}$ 0·9771, $n_{D}^{20°}$ 1·47633, $[R_L]_D$ 39·89 (calc., 39·51).

For the hydrolysis of large quantities of the semicarbazone it is better to use dil. H_2SO_4 instead of oxalic acid. When the semicarbazone was hydrolysed with 50% HCl aq. on the steam-bath, the ketone produced (and extracted in Et_2O) was accompanied by a colourless crystalline solid. The ketone was removed by steam-distillation, and the solid recrystallised from MeOH; prismatic plates, m. p. 150—152°. The substance formed a semicarbazone, m. p. 243°, gave *trans*-hexahydro-2-hydrindone when heated with dil. H_2SO_4 or HCl aq., and was possibly *di*-trans-*hexahydro-2-hydrindylidenehydrazine*, $C_8H_{14}{>}C{:}N{\cdot}N{:}C{<}C_8H_{14}$ (Found: C, 79·3; H, 10·3; N, 10·3. $C_{18}H_{28}N_2$ requires C, 79·4; H, 10·3; N, 10·3%).

Acids.

The hydroxy-ester (IV), prepared (Reformatsky) from *trans*-hexahydro-2-hydrindone 141 c.c., ethyl bromoacetate 112 c.c., C_6H_6 400 c.c., and Zn 70 g., had after redistillation b. p. 167°/20 mm., $d_{4°}^{20·2°}$ 1·0314, $n_{D}^{20·2°}$ 1·4729, $[R_L]_D$ 61·51 (calc., 61·13) (compare Kandiah, *loc. cit.*). A lower-boiling fraction and the residue gave the hydroxy-acid (III) on hydrolysis. The average yield of the hydroxy-ester was 50%; unchanged ketone, 25%; self-condensation product, 18%. In spite of its very high b. p., the last passed over in the lower fraction (120—160°/21 mm.) and was isolated from the unhydrolysed residue.

In later preps. of the hydroxy-ester the product of the Reformatsky reaction was hydrolysed (with cold 10% aq. alc. NaOH for 24 hrs.) after distillation of the C_6H_6, the uncondensed ketone, and some hydroxy-ester. In this way, the decomposition of the self-condensation product of the ketone was prevented and the yield of the hydroxy-acid improved.

The unhydrolysed residue gave the condensation product as a cryst. mass. This was washed with MeOH, in which it was sparingly sol. *trans*-Hexahydrohydrindylidenehexahydro-2-hydrindone crystallised from light petroleum (b. p. 60—80°) in aggregates of prismatic plates, m. p. 115—116° after shrinking (Kandiah, *loc. cit.*, p. 945, gives m. p. 126°) (Found : C, 83·6; H, 10·0. Calc. for $C_{18}H_{26}O$: C, 83·7; H, 10·1%). The *oxime*, formed readily by refluxing an alc. solution of the ketone with hydroxylamine hydrochloride in AcONa aq., crystallised from C_6H_6 in prismatic needles, m. p. 211—212° after sintering and turning brown (Found: C, 79·1; H, 9·8. $C_{18}H_{27}ON$ requires C, 79·1; H, 10%). A small quantity of oxime, obtained by dilution of the alc. mother-liquor, crystallised from C_6H_6–petroleum (b. p. 60—80°) in a network of flat needles, m. p. 206°.

The hydroxy-acid, whether obtained from the lower-boiling ester or the main fraction or the undistilled residual ester, crystallised from light petroleum (b. p. 60—80°) in rhombic plates, m. p. 87—88° (Kandiah gives m. p. 91°).

The hydroxy-acid (80 g.), 1·7*N*-alc. HCl (200 c.c.), and EtOH (400 c.c.), left at room temp. for 24 hrs., gave 80 g. of ester, b. p. 166—170°/20 mm.

Dehydration of the Hydroxy-acid (III).—The acid (30 g.) was boiled for 3 hrs. with Ac_2O (40 c.c.). No acetoxy-compound (IX) was obtained (compare Kandiah, *loc. cit.*). The crude acid was treated with Na_2CO_3 aq., the neutral product removed, and the acid obtained on acidification of the alkaline layer was crystallised from light petroleum (b. p. 60—80°); m. p. 151—152° (Kandiah, m. p. 155°). It had an iodine addition of 2·2% (10 mins.). This acid was obtained in considerable quantity by dehydration of the hydroxy-ester (IV).

The dibromide of the $\alpha\beta$-acid crystallised from light petroleum (b. p. 60—80°) in thick prismatic plates, m. p. 147—148° (Kandiah, m. p. 150°).

The *amide*, $C_8H_{14}{>}C{:}CH{\cdot}CO{\cdot}NH_2$, prepared from dry NH_3 and the acid chloride (b. p. 153—154°/16 mm.) in Et_2O, crystallised from C_6H_6 in rhombic plates, m. p. 154—155° (Found: C, 73·6; H, 9·4. $C_{11}H_{17}ON$ requires C, 73·7; H, 9·6%).

The acid chloride (2·5 g.) was decomposed with Na_2CO_3 aq. on the steam-bath. The cryst. product was extracted and dried in Et_2O and crystallised from light petroleum; plates, m. p. 116—118° (Found: C, 77·0; H, 8·6. $C_{22}H_{30}O_3$ requires C, 77·1; H, 8·8%). It was the *anhydride* of the $\alpha\beta$-acid (VII), which was partly reproduced on treating it with hot 10% Na_2CO_3 aq.

The iodine addition of the acid obtained from the acid chloride was 2·2%, the same as that of the pure $\alpha\beta$-acid.

Dehydration of the Hydroxy-ester (IV).—(i) *With phosphoric oxide.* When the ester was added to an excess of P_2O_5, much heat was generated and the ester distilled. The dark product was decomposed with H_2O and extracted with Et_2O. The dehydrated ester had b. p. 135—145°/11 mm. and *J* 30·3% (10 mins.), corresponding to 31% $\beta\gamma$-ester.

The hydroxy-ester (IV) was refluxed with an excess of P_2O_5 covered with dry C_6H_6 (6 vols.) for 4 hrs. The C_6H_6 was then distilled in vac., the ester drained off, and the residue worked up. The dehydrated ester (yield, 80%) after redistillation over a little P_2O_5 had b. p. 140—150°/11 mm. and *J* 33·7% (34·5% $\beta\gamma$-ester).

(ii) *With phosphorus oxychloride.* The hydroxy-ester (67 g.) was refluxed with $POCl_3$ (20 c.c.) and dry C_6H_6 (100 c.c.) for 2 hrs. and left over-night at room temp. The dark product was worked up. The dehydrated ester (45 g.; 72% yield) had b. p. 150—160°/20 mm. (Kandiah, b. p. 152°/15 mm.).

(iii) *With thionyl chloride* (Darzens, *loc. cit.*). The hydroxy-ester (90 g.) in pyridine (73 g.) was treated with thionyl chloride (31 c.c.). The product was left over-night, extracted in light petroleum (b. p. 40—60°) washed with H_2O, dil. HCl aq., Na_2CO_3 aq., NaOH aq., and H_2O. The dehydrated ester (76 g.; 92% yield) had b. p. 138—150°/12 mm., about 40 g. coming over at 142—143°/12 mm. The iodine addition of the ester (76 g.) was 41·3%, corresponding to 42% $\beta\gamma$-ester.

The unsaturated ester from the above dehydration experiments was hydrolysed with cold 10% aq. alc. NaOH for 24 hrs. The unhydrolysed part having been removed, the acid was crystallised from much light petroleum (b. p. 60—80°), the $\alpha\beta$-acid separating. The petroleum was evaporated from the mother-liquor in vac., and the residue (85 g.) partially esterified (Kon and Thakur's quantities) for 6 hrs. The ester was fractionally distilled : (i) 40 g., b. p. 132—135°/10 mm., (ii) 10 g., b. p. 135—138°/10 mm. (Kandiah, b. p. 144°/15 mm.); 34 g. of the acid were recovered.

The ester (i) was hydrolysed with cold 10% methyl-alcoholic NaOH for 24 hrs., the MeOH distilled in vac. below 35°, and the neutral portion eliminated. The *acid* crystallised from *n*-hexane at 0° in fine plates, m. p. 66—67° (Kandiah, *loc. cit.*, m. p. 144°) (Found : C, 73·1; H, 8·8; equiv., by titration, 180·2. $C_{11}H_{16}O_2$ requires C, 73·3; H, 9·0%; equiv., 180·1). Even on very careful hydrolysis, care being taken to preclude tautomeric change, the hydrolysed acid contained a small quantity of the $\alpha\beta$-acid. In such cases, the first crop of the acid was again partially esterfied; later crops, however, consisted of the pure $\beta\gamma$-acid.

The dibromide, $C_8H_{13}Br{>}CBr\cdot CH_2\cdot CO_2H$, prepared from the $\beta\gamma$-acid was obtained as a viscous solid on evaporation of the $CHCl_3$ in vac. It was ground with light petroleum and crystallised from C_6H_6–petroleum (b. p. 60—80°) or petroleum, forming rhombic plates, m. p. 135° (Kandiah, m. p. 146°) (Found : C, 38·7; H, 4·5. Calc. for $C_{11}H_{16}O_2Br_2$: C, 38·8; H, 4·7%). Mixed m. p. with the dibromide (m. p. 148°) obtained from the $\alpha\beta$-acid, 112°, clearing at 122°.

The *amide*, $C_8H_{13}{\geqslant}C\cdot CH_2\cdot CO\cdot NH_2$, formed from the undistilled $\beta\gamma$-acid chloride, crystallised from C_6H_6 in silky plates, m. p. 160—161° after sintering (Found: C, 73·6; H, 9·4. $C_{11}H_{17}ON$ requires C, 73·7; H, 9·6%). Mixed m. p. with the amide (m. p. 154—155°) of the $\alpha\beta$-acid, 125—128°.

Reference Curve.—The iodine additions (J) of the $\alpha\beta$, $\beta\gamma$-acids and their mixtures were determined by the method of Linstead and May (J., 1927, 2565), with the modifications described on p. 2132.

% $\alpha\beta$	0	10	25	50	60	70	80	90	100
J, %	77·2	71·1	62·8	52·1	46·4	39·6	30·8	17·9	2·2

Equilibrations.—The two acids, $\alpha\beta$ and $\beta\gamma$, were heated with KOH aq. The results are in Table I.

TABLE I.

Acid.	% KOH.	Temp.	Time (hrs.).	J, %.	Comp., % $\alpha\beta$.
$\beta\gamma$	25	100°	0·5	61·2	30
,,	,,	,,	1	56·9	40
,,	,,	,,	2	46·4	60
,,	,,	,,	3	29·5	81
,,	,,	,,	4	20·5	88
,,	,,	,,	6	13·7	93
,,	,,	,,	10	19·8	89
$\beta\gamma$	19	B. p.	23	21·3	87·5
$\alpha\beta$	25	100	6	13·7	93
	,,	,,	13	15·2	92
,,	,,	,,	24	14·5	92·5
,,	,,	B. p.	66	14·5	92·5
,,	,,	,,	96	17·3	90·5
,,	20	,,	359	17·3	90·5

Even after the acid (obtained on acidification of the KOH solution) had been heated with 10% Na_2CO_3 aq. for 15 mins. on the steam-bath, a small quantity remained unacted upon (compare Wechsler, *Monatsh.*, 1893, **14**, 462). On extraction of the alkaline liquid with Et_2O and evaporation of the solvent, it was identified as the $\alpha\beta$-acid, m. p. and mixed m. p. 151—152°.

The value at equilibrium may be taken as 90% *αβ*, a figure which is confirmed by the results of partially esterifying the fully equilibrated *αβ*-acid (see below). The equilibrated acid, either from the *αβ*- or the *βγ*-side, had m. p. 151—152° after crystallisation from C_6H_6.

When the results of equilibrations (comp. % *αβ* in the first four expts.) are plotted against time (hrs.), the points obtained lie on a straight line. This is probably due to the irregularity in the change caused by the sparing solubility of the potassium salts. The mobility, under the experimental conditions, is of the order of 6, and similarly the half-change period is about 75 mins.

Partial Esterification of the Equilibrated αβ-Acid.—The *αβ*-acid (138 g.) was boiled with KOH (250 g.) in H_2O (750 c.c.) in a copper flask for 3 days. The equilibrated acid obtained on acidification was boiled with light petroleum (b. p. 60—80°). Most of the unchanged *αβ*-acid was left undissolved, and more separated from the filtrate. The petroleum was evaporated from the mother-liquor in vac., and the residue partially esterified (Kon and Thakur's quantities). The ester (16·5 g.) had b. p. 140—141°/15 mm. (a very small quantity at 141—145°/15 mm.), $d_{4^\circ}^{16\cdot7^\circ}$ 0·9900, n_D 1·4770, and J 89·3%. The iodine value corresponds to 92% *βγ*-ester. The unesterified acid was mixed with the unchanged *αβ*-acid and the equilibration and subsequent partial esterification were repeated. From the several experiments, the percentage of *βγ*-acid in the equilibrated product worked out concordantly to about 10. The *βγ*-acid obtained from the hydrolysis of the above ester was identical with that mentioned above (m. p. 66—67°).

Esters.

Preparation of the αβ-Ester (V).—When the excess of NH_3 was being removed from the solution of the ammonium salt of the *αβ*-acid, a colourless solid separated which dissolved again on addition of a little more dil. NH_3 aq. (compare Part II, p. 2144). The ester, formed by refluxing the Ag salt with EtI in dry Et_2O, was washed with dil. NaOH aq. and H_2O. *Ethyl* trans-*hexahydrohydrindylidene-2-acetate* had b. p. 158°/19 mm.; $d_{4^\circ}^{17\cdot9^\circ}$ 1·0018, $n_D^{17\cdot9^\circ}$ 1·4938, whence $[R_L]_D$ 60·47 (calc., 59·21); J 0·4% (Found: C, 74·7; H, 9·5. $C_{13}H_{20}O_2$ requires C, 74·9; H, 9·7%). A second sample, similarly prepared, had $d_{4^\circ}^{20\cdot2^\circ}$ 1·0018, $n_D^{20\cdot2^\circ}$ 1·4924, and J 1·6% (10 mins.), 3·7% (30 mins.), and 75% (60 mins.).

Preparation of the βγ-Ester (VI).—The *βγ*-acid (24·3 g., m. p. 64—65°) was esterified for 7½ hrs. with *N*-alc. HCl (26 c.c.) and EtOH (62 c.c.). The mixture was diluted with much H_2O containing Na_2CO_3, and the ester extracted, washed (once with dil. NaOH aq. and then with H_2O), and dried in Et_2O. Ethyl *trans*-hexahydroindenyl-2-acetate had b. p. 133—135°/11—13 mm.; $d_{4^\circ}^{17\cdot9^\circ}$ 0·9884, $n_D^{17\cdot9^\circ}$ 1·4760, whence $[R_L]_D$ 59·42 (calc., 59·21); J 97% (10 mins.) (compare Kandiah, *loc. cit.*) (Found: C, 74·9; H, 9·6. Calc. for $C_{13}H_{20}O_2$: C, 74·9; H, 9·7%). Another sample had b. p. 140°/19 mm. $d_{4^\circ}^{19\cdot8^\circ}$ 0·9874, $n_D^{19\cdot8^\circ}$ 1·4758, $[R_L]_D$ 59·43, and J 97% (10 mins.).

Reference Curve.—

% *αβ*	0	10	20	30	40	50	60	70	80	90	100
J, % (10 mins.)	97	87·9	78·5	68·6	59·2	49·7	39·8	29·9	20·2	10·4	0·4

Equilibrations.—The *αβ*- and the *βγ*-ester were treated with *N*-NaOEt (prepared from Ca-dried EtOH) under Kon and Linstead's standard conditions: the results are in Table II.

TABLE II.

Expt.	Ester.	*N*-NaOEt.	Temp.	Time.	$d_{4°}^{t°}$.	$n_D^{t°}$.	*J*, %.	Comp., % αβ.
1	βγ	Theo	25°	2 mins.	0·9987/20°	1·4887	25·5	74
2	,,	,,	,,	5 ,,	1·0018/20	1·4921	7·3	93
3	,,	,,	,,	10 ,,	1·0017/20	1·4925	2	98·5
4	,,	,,	,,	20 ,,	1·0018/20	1·4925	2	98·5
5	,,	,,	,,	30 ,,	—	1·4927	2	98·5
6	,,	,,	,,	60 ,,	—	1·4941	4	96·5
7	,,	,,	,,	90 ,,	—	1·4939	4	96·5
8	,,	Excess	,,	120 ,,	—	1·4937	2·6	98
9	αβ	,,	,,	2 hrs.	—	—	1·6	99
10	,,	,,	,,	4 ,,	—	—	1·6	99
11	,,	,,	100	2 ,,	1·0018/19·7	1·4932	2·7	98

In Expts. 1 and 2, βγ-ester having *J* 92·6% (95% βγ) was used.

In Expt. 8, βγ-ester having *J* 87·9% (90% βγ) was used.

The point of equilibrium is about 98·5 ± 0·5% αβ. The half-change period is much less than 2 mins. On account of the error introduced by using short intervals of time (*e.g.*, 2 mins. and 5 mins.), the value of mobility, $10^4 \times (k_1 + k_2)$ min.$^{-1}$, can be estimated only approximately and is greater than 5000.

The yield of the equilibrated ester was more than 80% in every case, and the b. p. never exceeded that of the pure αβ-ester, being always about 148°/11 mm. On account of tho short duration of the treatment of the esters with NaOEt, there could be no question of the formation of the ethoxy-ester. The βγ-ester from expt. 7 was analysed (Found : C, 74·7; H, 9·5. $C_{13}H_{20}O_2$ requires C, 74·9; H, 9·7%. The ethoxy-ester, $C_{15}H_{26}O_3$, requires C, 70·9; H, 10·2%).

The equilibrated βγ-ester gave on oxidation *trans*-hexahydro-2-hydrindone, which was identified by its characteristic smell and its semicarbazone (m. p. and mixed m. p. 243°). The acid from the hydrolysis of the equilibrated βγ-ester was crystallised from C_6H_6; it had m. p. 151—152° and was identified as the αβ-acid (VII).

Ketones.

trans-*Hexahydrohydrindylidene*-2-*acetone* (X).—The αβ-acid chloride was converted by ZnMeI into the ketone, which was purified through its semicarbazone, m. p. 221—222° (decomp.) (Kandiah, J., 1931, 972, gives m. p. 218°), and regenerated therefrom by steam-distillation with oxalic acid (it is not easily volatile in steam); it then had b. p. 134°/10 mm.; $d_{4°}^{20°}$ 0·9738, $n_D^{20°}$ 1·5047, whence $[R_L]_D$ 54·11 (calc., 52·32); *J* 5·5% (5 mins.), 7·7% (10 mins.).

Ozonisation of the Ketone.—The ketone in AcOEt was treated with ozonised oxygen at 0°, the ozonide freed from the solvent and decomposed, and the product steam-distilled. The residue crystallised from dil. Me_2CO in stout gritty crystals, m. p. 157—158° clearing at 160°, identified as *trans*-hexahydrohomophthalic acid. From the aqueous distillate Et_2O extracted *trans*-hexahydro-2-hydrindone, b. p. 80—84°/9 mm. (semicarbazone, m. p. and mixed m. p. 243° decomp.).

Attempts to prepare trans-*Hexahydroindenyl*-2-*acetone*.—The βγ-acid chloride (prepared from the βγ-acid and thionyl chloride, the excess of the latter being removed in vac. below 30°) was converted by ZnMeI into a ketonic product. This was not distilled but, after removal of the solvents, was converted into the semicarbazone, m. p. (without purification) and mixed m. p. (with the $\alpha\beta$-semicarbazone) 215—216°. The acid obtained from the alkaline washing of the above product was crystallised from hexane; m. p. 66—75° (m. p. of pure $\beta\gamma$-acid, 66—67°).

The $\alpha\beta$-ketone (X) (6 g.) reacted vigorously with "molecular" Na (0·8 g.) under dry Et_2O, but some Na remained after 3½ hrs. The orange-red liquid was quickly filtered and cooled to $-40°$, and a cooled solution of the calc. quantity of dry $PhCO_2H$ in dry Et_2O added (compare Hugh and Kon, *loc. cit.*). $PhCO_2Na$ was instantly pptd. The filtered liquid was worked up, and the ether evaporated in vac. at room temp. The residue gave a semicarbazone, m. p. 195—197°, and 212—213° after crystn. from MeOH (Found: C, 66·5; H, 8·9. Calc. for $C_{13}H_{21}ON_3$: C, 66·4; H, 8·9%), which did not depress the m. p. (222°) of the $\alpha\beta$-semicarbazone. A small quantity of a more sol. semicarbazone, m. p. 178—181°, was also isolated.

Equilibrations.—The $\alpha\beta$-ketone (6·2 g.) was treated with an excess of approx. *N*-NaOEt for 10 and 30 mins., respectively, at 25°. About 86% of the material was recovered. The first sample had b. p. 132°/10 mm., $d_{4°}^{20°}$ 0·9745, $n_D^{20°}$ 1·5046, and *J* 5·7% (10 mins.); the second had b. p. 131°/10 mm., $d_{4°}^{20°}$ 0·9743, $n_D^{20°}$ 1·5047, and *J* 5·5%. The semicarbazone from these melted at 218° (decomp.) without any purification.

Condensation with Ethyl Sodiomalonate.—The $\alpha\beta$-ketone (X) (4·5 g.) was heated with ethyl malonate (4 g.) and Na (0·58 g.) in EtOH (18 c.c.) for 10 hrs. on the steam-bath (compare Norris and Thorpe, J., 1921, **119**, 1199), and the product was diluted with H_2O and acidified. *Ethyl* cyclo*hexane*-3 : 5-*dione*-1(2′)-spiro-trans-*hexahydrohydrindene*-2-*carboxylate* (7·2 g.), isolated by means of Et_2O, crystallised from AcOEt–petroleum or C_6H_6–petroleum in prismatic needles, m. p. 156—157° (Found: C, 69·6; H, 8·1. $C_{17}H_{24}O_4$ requires C, 69·8; H, 8·2%). Hydrolysis of this ester with 20% KOH aq. on the steam-bath for 3½ hrs. gave *cyclo*hexane-3 : 5-dione-1(2′)-*spiro-trans*-hexahydrohydrindene, m. p. 199—200° (decomp.) (compare Kandiah, *loc. cit.*, p. 973) (Found: C, 76·2; H, 8·9. Calc. for $C_{14}H_{20}O_2$: C, 76·4; H, 9·1%).

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