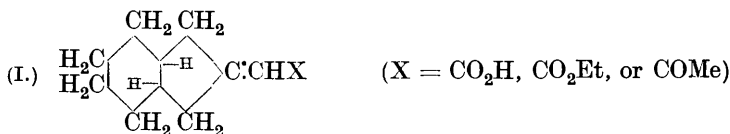


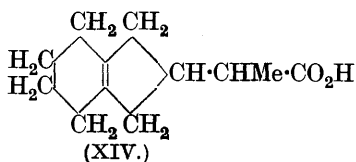
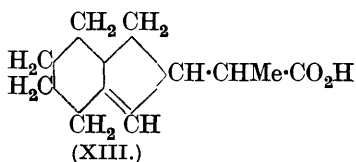
300. *Three-carbon Tautomerism in Dicyclic Systems. Part IV. The Effect of an α -Methyl Group on Tautomerism in trans-Hexahydrohydrindene Compounds.*

By R. S. THAKUR.

THIS paper deals with the effect of an α -methyl group on the tautomeric mobility and position of equilibrium in the system (I).



reason for the abnormal result must be sought in the nature of the $\beta\gamma$ -acid (VIII). Experiment shows that this must contain some 25% of an isomeride. For instance, if the original $\beta\gamma$ -acid is treated with aqueous potash to convert the $\beta\gamma$ -acid contained in it into the $\alpha\beta$ -, and the mixture is then partly esterified, the ester formed contains the whole of the isomeride. On hydrolysis this is obtained as a solid, m. p. 88° . It has a high iodine addition, which is practically unchanged when the acid is boiled with aqueous potash for a long time. The position of the double bond in it, either Δ^3 or Δ^8 (XIII or XIV), has not yet been determined.



As the potassium salt of the $\alpha\beta$ -acid is sparingly soluble in boiling aqueous potash, and as scarcely 4% of the $\beta\gamma$ -acid is present in the fully equilibrated acid, all attempts to prepare the pure $\beta\gamma$ -acid from the $\alpha\beta$ -acid in this way failed. There can, however, be no doubt as regards the position of equilibrium being 96% $\alpha\beta$, as the results of equilibrations of mixtures of the $\alpha\beta$ - and the $\beta\gamma$ -acid show.

Esters.—The $\alpha\beta$ - and the $\beta\gamma$ -ester (V and VI) were equilibrated under Kon and Linstead's conditions (J., 1929, 1269). The discrepancy between the two series of results (Table III) is seen, when mixtures of the two esters are equilibrated, to be due to the presence of an isomeric impurity in the $\beta\gamma$ -ester. The equilibrium is completely on the side of the $\alpha\beta$ -ester. As the $\beta\gamma$ -ester could not be obtained in a pure state, the mobility can only be estimated and is of the order of 450.

Ketones.—The position of equilibrium is coincident with the pure $\alpha\beta$ -ketone, since no change is observed in its physical properties and iodine addition on treating it with sodium ethoxide. No estimate of mobility is possible, but it is presumably very high.

The above results are summarised in Table I, those for other cyclic compounds $(\text{CH}_2)_n > \text{C}:\text{CRX}$ being recorded for comparison (with these should be compared the values given on p. 2127).

The results in cols. 2 and 3 show that (1) the α -methyl group considerably retards the mobility of the *trans*-hexahydrohydrindene esters and shifts the position of equilibrium to the $\alpha\beta$ -side: in the *trans*- β -decalin esters the shift is to the $\beta\gamma$ -side; (2) the retarding effect is also observed in the acids and the equilibrium has been shifted towards the $\alpha\beta$ -side; (3) in the ketones, the equilibrium is still coincident with the pure $\alpha\beta$ -ketone; the effect on the mobility is uncertain.

TABLE I.

	<i>trans</i> -2-C ₈ H ₁₄ >C.		<i>n</i> = 4,	<i>n</i> = 5,	<i>trans</i> -β-
	R = H.	R = Me.	R = Me.	R = Me.	C ₆ H ₁₀ >C, R = Me.
X = CO ₂ H.					
Eqm. % αβ	90	96	38 ²	32 ²	
Mobility			0.58	0.0075	
X = CO ₂ Et.					
Eqm. % αβ	98	100	88 ¹	5 ¹	10
Mobility	>5000	ca. 450	84	0.15	0.05
X = COMe.					
Eqm. % αβ	100	100	64 ²	0 ²	0
Mobility	—	—	3000	—	

very high

¹ Private communication from Dr. G. A. R. Kon, Dr. R. P. Linstead, and Mr. G. W. G. MacLennan. ² Kon and Thakur, J., 1930, 2217.

The most striking point emerging from these results is that, whereas the introduction of an α-methyl group in a neutral system, including those described in Part II, shifts the equilibrium towards the βγ-side (Abbott, Kon, and Satchell, J., 1928, 2514; Kon and Thakur, *loc. cit.*; Kon and Leton, J., 1931, 2496), this has not been observed in the present investigation; indeed, the displacement, although small, is in the opposite sense.

From the above table, and that on p. 2127, it would appear that in tautomeric mobility and position of equilibrium the compounds of *trans*-β-decalin resemble those of *cyclohexane* more than the compounds of *trans*-hexahydrohydrindene do those of *cyclopentane*. In other words, the fusion of a *cyclohexane* ring in the 1:2-*trans*-position to another *cyclohexane* or *cyclopentane* ring does not produce the same results—some factor or factors are brought into play to an unequal extent in the two series. No explanation can be put forward for this difference. It is equally difficult to explain the very high mobility of the *trans*-hexahydrohydrindene compounds. It would be unsound to consider the existence of strain in the latter (discussed in Part III) as partly responsible for the difference until the results of a similar study of the *cis*-hexahydrohydrindene compounds are available.

At one time the preponderance of the αβ-form in equilibrium mixtures of such compounds as ethyl α-cyanocyclohexylideneacetate and the unsaturated nitriles was explained by the greater conjugative power of the nitrile group in comparison with other "activating" groups (Birch, Kon, and Norris, J., 1923, 1361; Linstead, J., 1929, 2498). In the hexahydrohydrindene compounds studied, no such "conjugation" factor can be present, yet the tautomeric equilibria are completely on the αβ-side.

Brief reference may be made to the isomerisation of the acid chlorides of the unsaturated acids on distillation (compare Johnson

and Kon, J., 1926, 2748). In the *trans*- β -decalin series the $\alpha\beta$ -acid chloride tends to pass into the $\beta\gamma$ -isomeride, but in the *trans*-hexahydrohydrindene acids this tendency is reversed. It is an open question, however, whether this isomeric change is brought about by distillation alone or by a trace of hydrochloric acid present.

During the present investigation, the various compounds of the general type $C_8H_{14} > C < \begin{matrix} X \\ Y \end{matrix}$ have been isolated in one form only. Similarly, no isomerism was encountered when X and Y were replaced by a symmetrical or an unsymmetrical ring (compare Kandiah, *loc. cit.*). This is in harmony with, and lends support to, the views of Hückel and Friedrich (*Annalen*, 1926, 451, 132) that the cyclopentane ring is symmetrically placed with respect to the rest of the molecule.

EXPERIMENTAL.

Acids.

Condensation of trans-Hexahydro-2-hydrindone with Ethyl α -Bromopropionate.

—The ketone (282 c.c.), ethyl α -bromopropionate (252 c.c.), Zn (140 g.), and C_6H_6 (800 c.c.) were refluxed on the steam-bath. The product was decomposed with ice-cold H_2O and dil. H_2SO_4 , and the aq. layer extracted once with light petroleum (b. p. 40–60°) instead of Et_2O (this process facilitates considerably the separation of the aq. layer in subsequent washings). After removal of the solvents under diminished pressure, the product was distilled until about 50 g. of the hydroxy-ester had been collected (b. p. 163°/15 mm.). The distilled fraction and the ester left in the distilling flask were hydrolysed separately with cold 10% aq. alc. NaOH for 24 hrs.

2-Hydroxy- α -methyl-trans-hexahydrohydrindene-2-acetic acid (III), obtained from the distilled ester, crystallised from C_6H_6 -petroleum or C_6H_6 in plates, m. p. 119–120° (Found: C, 67.6; H, 9.4; equiv., by titration, 211.9. $C_{13}H_{20}O_3$ requires C, 67.9; H, 9.5%; equiv., 212.2). The acid obtained by hydrolysis of the bulk of the ester had the same m. p. Total yield of the hydroxy-acid, 84%.

Esterification of the Hydroxy-acid (III).—(i) *By alcoholic hydrogen chloride.* A mixture of the hydroxy-acid (212 g.), EtOH (250 c.c.), and 2.4*N*-alc. HCl (250 c.c.), left for 8 days at room temp., gave 10 g. of unchanged acid, 2 g. of a liquid, b. p. below 155°/11 mm., and 211 g. of ester, b. p. 156–157°/11 mm., d_4^{20} 1.0246, n_D^{20} 1.4727, $[R_L]_D$ 65.32.

After the hydroxy-acid (478 g.), EtOH (400 c.c.), and 1.7*N*-alc. HCl (450 c.c.) had been heated on the steam-bath for 39 hrs., the usual treatment gave 48 g. of unchanged acid and 459 g. of ester, b. p. 155–156°/10 mm., d_4^{20} 1.0172, n_D^{20} 1.4766, $[R_L]_D$ 66.68 (calc., 65.73).

(ii) *Ethyl 2-hydroxy- α -methyl-trans-hexahydrohydrindene-2-acetate* prepared from the Ag salt had b. p. 154°/10 mm., d_4^{20} 1.0196, n_D^{20} 1.4710, $[R_L]_D$ 65.85 (calc., 65.73) (Found: C, 69.8; H, 9.9. $C_{14}H_{24}O_3$ requires C, 70.0; H, 10.0%).

Dehydration of the Hydroxy-acid with Acetic Anhydride.—The hydroxy-acid (53 g.) was boiled with Ac_2O (72 c.c.) for 3 hrs., H_2O added, the excess of Ac_2O removed under diminished pressure, and the residue treated with hot Na_2CO_3 aq. The alkaline solution, after being shaken with Et_2O , was acidified. The

pptd. *α-methyl-trans-hexahydrohydrindylidene-2-acetic acid* (VII) was extracted in much Et_2O ; it crystallised from C_6H_6 in clusters of small needles, m. p. 196—197°, J 0.6% (10 mins.) (Found: C, 74.0; H, 9.1; equiv., by titration, 193.7. $\text{C}_{12}\text{H}_{18}\text{O}_2$ requires C, 74.2; H, 9.3%; equiv., 194.2), sparingly sol. in petroleum.

As the $\alpha\beta$ -acid dissolved with difficulty in Na_2CO_3 aq., some of it passed in the ethereal extract along with the neutral portion; from this it was recovered, m. p. 196—197°.

The $\alpha\beta$ -acid (VII) (3 g.), dissolved in much NaHCO_3 aq., was oxidised at 0° with 3% KMnO_4 aq. The alkaline liquid, on extraction with Et_2O , gave *trans-hexahydrohydrindone*, b. p. 88—90°/9 mm., identified by its characteristic odour and by the formation of its semicarbazone, m. p. 245°.

The *methyl ester* (IX), obtained by refluxing the Ag salt of the $\alpha\beta$ -acid with MeI in Et_2O , solidified on evaporation of the solvent; it crystallised from MeOH or hexane at 0° in large rhombic plates, m. p. 43—45° (Found: C, 75.1; H, 9.5. $\text{C}_{13}\text{H}_{20}\text{O}_2$ requires C, 75.0; H, 9.7%).

The *amide*, $\text{C}_8\text{H}_{14} > \text{C}:\text{Me}:\text{CO}:\text{NH}_2$, formed from NH_3 and the acid chloride (b. p. 163°/10 mm.) in Et_2O , crystallised from C_6H_6 in thin needles, m. p. 205° (Found: C, 74.4; H, 9.7. $\text{C}_{12}\text{H}_{19}\text{ON}$ requires C, 74.6; H, 9.8%).

The *dibromide*, $\text{C}_8\text{H}_{14} > \text{CBr}:\text{CBrMe}:\text{CO}_2\text{H}$, prepared from the $\alpha\beta$ -acid (1.94 g.) and Br (0.5 c.c.) in CHCl_3 , crystallised from C_6H_6 in blades and from CHCl_3 in rhomboid plates, m. p. 182—183° (decomp.) (Found: C, 40.4; H, 4.9. $\text{C}_{12}\text{H}_{18}\text{O}_2\text{Br}_2$ requires C, 40.7; H, 5.1%).

Dehydration of the Hydroxy-ester (IV).—(i) *With phosphoric oxide*. The hydroxy-ester (250 g.) was left with P_2O_5 (223 g.) under C_6H_6 (800 c.c.) for 3 hrs. at room temp. and then heated on the steam-bath for 4 hrs. The C_6H_6 was removed under diminished pressure, the ester decanted, and the black residue decomposed with ice and H_2O and extracted with Et_2O . The extract and the decanted ester were washed with dil. alkali and H_2O and dried. The dehydrated ester (213 g.; 93% yield) had b. p. 146—154°/9 mm., n_D^{20} 1.4866, J 49.9%, whence the $\beta\gamma$ (?)-ester content is 45%.

(ii) *With thionyl chloride*. To the hydroxy-ester (120 g.), dissolved in pyridine (81 c.c.), thionyl chloride (39 c.c.) was added drop by drop, and the whole left over-night. (In all the foregoing dehydrations, 2 mols. of pyridine were used instead of 1 mol. by mistake.) The product, worked up in the way already described (p. 2153), gave 104 g. (94% yield) of dehydrated ester which, after redistillation, had b. p. 141—154°/9 mm.; d_4^{20} 0.9909, n_D^{20} 1.4856, whence $[R_L]_D$ 64.33 (calc., 63.81); J 48.9% (10 mins.), whence $\beta\gamma$ -ester content = 44%.

Hydrolysis of the Unsaturated Ester.—The ester (365 g., b. p. 140—155°/9 mm.) was hydrolysed with 10% aq.-alc. NaOH for 48 hrs. at room temp., the unhydrolysed ester (190 g.; about 52%) removed, and the acid crystallised from C_6H_6 -petroleum. The $\alpha\beta$ -acid (VII) separated and more was obtained from the mother-liquor. The acid remaining after evaporation of the solvents was treacly.

Partial Esterification.—The above liquid acid (130 g.), EtOH (322 c.c.), and N -alc. HCl (140 c.c.) were left for 48 hrs. at room temp., 70 c.c. of 15% Na_2CO_3 aq. and some H_2O were then added, and the EtOH was removed under diminished pressure. The unesterified acid (50 g., obtained on acidification of the alkaline layer) gave more $\alpha\beta$ -acid on trituration with light petroleum. The ester was fractionally distilled: (i) 63 g., b. p. 135°/10 mm.; (ii) 16 g., b. p. 136—137°/10 mm.; (iii) 6 g., b. p. 137—140°/10 mm. After redistillation, (i)

had b. p. 135°/10 mm.; d_4^{20} 0.9776, n_D^{20} 1.47496, whence $[R_L]_D$ 63.98 (calc., 63.81); J 82.8% (10 mins.), 89.5% (30 mins.), 93.3% (60 mins.). Hence it contained about 89% of the $\beta\gamma$ -ester.

The above ester (76 g., b. p. 135—137°/10 mm.) was hydrolysed with cold 10% NaOH solution (80 c.c. of 40% NaOH aq. and the rest MeOH). After 36 hrs., the MeOH was removed below 35° under diminished pressure, and the residue worked up in the usual way; 57 g. of solid $\alpha\beta$ -acid and 14 g. of unhydrolysed matter were obtained. The latter was distilled: (i) 1.5 g., b. p. 130—146°/10 mm.; (ii) 12 g., b. p. 148—149°/10 mm. Both fractions crystallised, and separated from *n*-hexane in plates, m. p. 43—45°. The substance was identified as the methyl ester (IX) of the $\alpha\beta$ -acid by hydrolysis to the $\alpha\beta$ -acid, m. p. and mixed m. p. 196—197° (Found: C, 74.8; H, 9.6. Calc. for $C_{13}H_{20}O_2$: C, 75.0; H, 9.7%).

The unchanged liquid acid from the above partial esterification was shaken with cold $NaHCO_3$ aq. The alkaline solution, after extraction with Et_2O , gave an acid, b. p. 167—169° (decomp.)/10 mm. and 154—155°/1—2 mm. This was impure *a-methyl-trans-hexahydroindenyl-2-acetic acid* (Found: C, 73.9; H, 9.0; equiv., by titration, 194.3. $C_{12}H_{18}O_2$ requires C, 74.3; H, 9.1%; equiv., 194.2).

Reference Curve.—The iodine additions (J) of the $\alpha\beta$ - and $\beta\gamma$ -acids and their mixtures were determined by the method of Linstead and May (J., 1927, 2565), with the modifications already described (p. 2132). The solution of the $\beta\gamma$ -acid was slightly turbid, probably on account of slight decomposition during distillation. Moreover, it contained the isomeric impurity mentioned above, which had nearly the same high iodine addition.

% $\alpha\beta$	0	10	25	50	75	90	100
J , %	90	84.5	74.5	54.8	30.9	13.6	1

Equilibrations.—The $\alpha\beta$ - and $\beta\gamma$ -acids and their mixtures were heated with KOH aq. The results are in Table II.

TABLE II.

Expts.	Acid.	KOH, %.	Temp.	Time, hrs.	M .	J , %.	Comp., % $\alpha\beta$.
1	$\beta\gamma$	[10] \times 25	100°	20		85.5	8.5
2	"	"	"	45		73.8	26
3	"	"	"	102		59.1	45
4	"	"	"	170		50.1	56
5	"	"	"	266		47.7	59
6	"	[15] \times 20	B. p.	100		44.3	62.5
7	"	[15] \times 21	"	117		41.3	65
8	6 & 7	[16] \times 25	"	168		44.4	62.5
9	$\beta\gamma$	[20] \times 25	"	292	194.3	44.4	62.5
10	$\alpha\beta$	[20] \times 18	"	75	194.7	5.9	96
11	"	[20] \times 18	"	96	194.7	5.8	96
12	"	[34] \times 25	"	292	194.3	5.8	96
13	13% $\beta\gamma$ 87% $\alpha\beta$	[20] \times 25	"	65		9.7	93
14	30.5% $\beta\gamma$ 69.5% $\alpha\beta$	"	"	"		15	88
15	50% $\beta\gamma$ 50% $\alpha\beta$	"	"	"		19	85

The $\beta\gamma$ -acid used in the last three expts. had b. p. 153°/1 mm. and did not give a pure amide.

The recovery of the equilibrated acid in all cases was very good, exceeding

85—90%. In certain expts., all the $\alpha\beta$ -acid in the equilibrated acid mixture could not be made to react with Na_2CO_3 aq. and some of it passed into the ethereal solution on extraction: when recovered, it had m. p. 195—196°.

It is clear from the results that boiling KOH aq. does not produce any structural change in the acids other than that from $\beta\gamma$ to $\alpha\beta$ or vice versa. The rate of change of these acids is much slower than that of the unsubstituted acids (compare p. 2154). The position of equilibrium is about 96% $\alpha\beta$.

Isolation of the Isomeric Impurity (XIII or XIV).—The liquid $\beta\gamma$ -acid partly crystallised after distillation. The solid acid (m. p. 64—72°) was removed, and the filtrate (14 g.) boiled with KOH aq. for 64 hrs. The acid recovered from the alkaline liquid was treated with hot Na_2CO_3 aq., 0.9 g. of the $\alpha\beta$ -acid remaining undissolved. The acid (12.8 g.) was again recovered and ultimately, by trituration with hot hexane and partial esterification, 1.49 g. of the acid (XIII or XIV) were obtained, J 79.5% (Found: equiv., 193.7. $\text{C}_{12}\text{H}_{18}\text{O}_2$ requires equiv., 194.2).

This acid, however, was best obtained by partial esterification of the solid acid, m. p. 64—72°, or of the fully equilibrated $\beta\gamma$ -acid. The ester thus obtained was treated with an excess of approx. N -NaOEt for 1 hr. to convert the $\beta\gamma$ - into the $\alpha\beta$ -ester and was then hydrolysed. The $\alpha\beta$ -acid was easily removed on account of its sparing solubility. The acid (XIII or XIV) crystallised from hexane in clusters of prismatic needles, m. p. 89—90° after sintering (Found: C, 73.9; H, 9.1; equiv., by titration, 193.7. $\text{C}_{12}\text{H}_{18}\text{O}_2$ requires C, 74.2; H, 9.3%; equiv., 194.2). The *amide* crystallised from AcOEt—petroleum (b. p. 60—80°) in flat needles or thin plates, m. p. 185—186° after sintering (Found: C, 74.3; H, 9.7. $\text{C}_{12}\text{H}_{19}\text{ON}$ requires C, 74.6; H, 9.9%).

Esters.

Preparation of Ethyl α -Methyl-trans-hexahydrohydrindylidene-2-acetate (V).—The NH_4 salt of the $\alpha\beta$ -acid (VII) was very sparingly sol. in H_2O , crystallising even from a hot solution. *Ethyl α -methyl-trans-hexahydrohydrindylidene-2-acetate*, formed by the action of EtI on the Ag salt, had b. p. 154°/10 mm.; d_4^{20} 1.0014, n_D^{20} 1.4963, whence $[R_L]_D$ 64.85 (calc., 63.81); J 0.8% (10 mins.) (Found: C, 75.5; H, 9.8. $\text{C}_{14}\text{H}_{22}\text{O}_2$ requires C, 75.6; H, 10.0%).

Ethyl α -methyl-trans-hexahydroindenyl-2-acetate (VI) was obtained by partial esterification of the liquid $\beta\gamma$ -acid for 8 hrs. After redistillation it had b. p. 134°/10 m.; d_4^{20} 0.9792, n_D^{20} 1.4748, whence $[R_L]_D$ 63.86 (calc., 63.81); J 87.8% (10 mins.) (Found: C, 75.4; H, 9.9. $\text{C}_{14}\text{H}_{22}\text{O}_2$ requires C, 75.6; H, 10.0%). This ester contained about 10% of an isomeric ester (not $\alpha\beta$ -ester).

Reference Curve.—

% $\alpha\beta$	0	10	20	30	40	50
J , % (10 mins.)	87.8	83.7	78.8	72.3	64.2	55
% $\alpha\beta$	60	70	80	90	100	
J , % (10 mins.)	45.1	34.7	23.5	12.3	0.4	

Equilibrations.—The $\alpha\beta$ -, $\beta\gamma$ -esters and their mixtures were treated with NaOEt in Ca-dried EtOH. The results are in Table III.

The recovery of the esters exceeded 80% in all cases and the b. p. was never higher than that of the pure $\alpha\beta$ -ester. The physical properties and the iodine addition of the $\alpha\beta$ -ester are scarcely changed by treatment with NaOEt. The lower refraction of the fully equilibrated $\beta\gamma$ -ester is noteworthy, indicating the presence of the isomeric unsaturated impurity. The position of equilibrium

is 100% $\alpha\beta$. As the $\beta\gamma$ -ester was not quite pure in the above experiments, the value of the mobility, $10^4 \times (k_1 + k_2)$ min.⁻¹, is approx. 450 and represents a lower limit. The half-change period, from the mobility curve, is about 15 mins.

TABLE III.

Ester. $\beta\gamma$	N-NaOEt. Theo.	Temp. 25.3°	Time,		J , %.	Comp., % $\alpha\beta$.	
			hrs.	d_4^{20} .			
			0.17	0.9873	1.4829	64.8	39.5
			0.33	0.9928	1.4872	45.1	60
			0.5	0.9956	1.4902	31.7	73
			0.66	0.9982	1.4921	22.3	81
			1	0.9998	1.4938	16	86.5
			1.5	1.0004	1.4942	14	88.5
			3	1.0002	1.4936	18.3	85
			4	1.0011	1.4946	12	90
	Excess		13	1.0004	1.4947	10.8	91
	Theo.		18	1.0011	1.4946	12	90
$\alpha\beta$			0.33	1.0007	1.4962	1.3	99.5
			0.66	1.0008	1.4961	0.9	99.7
			3	1.0007	1.4962	0.9	99.7
			16	1.0007	1.4962	0.9	99.7
			20	1.0008	1.4961	0.4	100
		100	0.5	1.0014	1.4962	0.8	99.5
			1	1.0014	1.4962	0.8	99.5
49.7% $\alpha\beta$	Excess	25.3	6	1.0002	1.4949	8.9	92.5
50.3% $\beta\gamma$							
69.7% $\alpha\beta$	"	"	"	1.0008	1.4958	3.9	97
30.3% $\beta\gamma$							
90.4% $\alpha\beta$	"	"	"	1.0007	1.4960	2.9	98
9.6% $\beta\gamma$							

In Expt. 15, the $\alpha\beta$ -ester recovered from Expts. 16 and 17 was used.

Ketones.

a-Methyl-trans-hexahydrohydrindylidene-2-acetone (XI).—*a*-Methyl-trans-hexahydrohydrindylidene-2-acetic acid (32 g.) was treated with thionyl chloride (18 c.c.) at room temp. and later for 15 mins. on the steam-bath. On removal of the excess of thionyl chloride under diminished pressure, the acid chloride crystallised; b. p. 163°/10 mm., m. p. 40—115° owing to conversion into the $\alpha\beta$ -acid in air. The acid chloride in dry toluene was treated with ZnMeI in the usual way. After decomposition with ice, the product was diluted with Et₂O, and the filtered solution washed successively with sat. (NH₄)₂SO₄ aq., very dil. NaOH aq., H₂O, dil. HCl aq., and H₂O and dried. After evaporation of the solvents, the ketonic product (80% yield) distilled at 148°/10 mm. and readily gave a *semicarbazone*, m. p. 206°, which was sparingly sol. in all solvents and separated from MeOH in very small crystals, m. p. 206—208° (decomp.) (Found : C, 67.5; H, 9.2. C₁₄H₂₂ON₃ requires C, 67.4; H, 9.3%). The alkaline washings gave the $\alpha\beta$ -acid (VII).

The *ketone* (XI) regenerated from the *semicarbazone* by steam-distillation with oxalic acid had b. p. 144—148°/9 mm.; d_4^{20} 0.9839, n_D^{20} 1.5120, whence $[R_L]_D$ 58.61 (calc., 57.53); J 1.8% (5 mins.), 2.6% (10 mins.) (Found : C, 81.1; H, 10.2. C₁₃H₂₀O requires C, 81.3; H, 10.4%). The *ketone* was sparingly volatile in steam and was not completely regenerated with oxalic acid. In later regenerations, therefore, hot dil. H₂SO₄ was used and the *ketone* was extracted with Et₂O.

Ozonisation. The *ketone* (XI) in CHCl₃ was treated with ozonised oxygen

at 0°, and the ozonide freed from the solvent. *trans*-Hexahydro-2-hydrindone (b. p. 87—92°/10 mm.; semicarbazone, m. p. and mixed m. p. 243°) was isolated by steam-distillation of the ozonide and subsequent extraction with Et₂O. The residue from the steam-distillation was neutral to litmus, insol. in hot H₂O, and very sparingly sol. in EtOH; it crystallised from light petroleum (b. p. 60—80°) in fern-shaped crystals, m. p. 194—195° (violent decomp.) [Found: C, 69.8; H, 8.8. (C₉H₁₄O₂)_n requires C, 70.1; H, 9.1%] and appeared to be the *peroxide* of *trans*-hexahydro-2-hydrindone.

Condensation with ethyl sodiomalonate. The ketone (XI) (3.84 g.) was refluxed with ethyl malonate (3.2 g.) and NaOEt (0.46 g. Na in 14 c.c. EtOH) for 2 days. The uncondensed ketone gave the semicarbazone (4 g.), m. p. 204—205° (decomp.). The dihydroresorcinol ester was a reddish-brown viscous mass, and on hydrolysis with 20% KOH aq. 2-methylcyclohexane-3 : 5-dione-1(2')-spiro-*trans*-hexahydrohydrindene (XII) (0.6 g.) was obtained, which crystallised from C₈H₆-petroleum (b. p. 60—80°) in rectangular plates, m. p. 164—165° (Found: C, 76.8; H, 9.3. C₁₅H₂₂O₂ requires C, 76.9; H, 9.4%).

Attempt to prepare the βγ-Ketone (compare Hugh and Kon, *loc. cit.*).—The sodio-derivative of the αβ-ketone (XI) (6.6 g.) was treated with benzoic acid as described on p. 2157. The product gave a *semicarbazone*, m. p. 213°, and 222° after recrystn. from EtOH, which did not depress the m. p. of the semicarbazone of the parent ketone nor that of the semicarbazone of *trans*-hexahydrohydrindylidene-2-acetone (Found: C, 67.0; H, 9.0. C₁₄H₂₂ON₃ requires C, 67.4; H, 9.3%). The ketone regenerated from the semicarbazone with dil. H₂SO₄ decolorised alkaline KMnO₄ aq., the odour of *trans*-hexahydro-2-hydrindone becoming perceptible.

In another experiment in which the benzoic acid solution was added to the sodio-derivative of the ketone (XI) (6 g.) without filtration of the residual Na, the smell of the product was quite unlike that of the parent ketone. The semicarbazone was boiled with MeOH: the residue had m. p. 203—206° and was evidently derived from the parent ketone; the solution deposited plates, m. p. 180—183°. After recrystallisation the *semicarbazone* of *trans*-hexahydrohydrindyl-2-acetone had m. p. 180° after sintering (Found: C, 67.0; H, 10.0. C₁₄H₂₂ON₃ requires C, 66.9; H, 10.0%). It depressed the m. p. of the βγ (?)-semicarbazone (m. p. 172°) obtained by methylation (mixed m. p. 146—152°).

Methylation of trans-Hexahydrohydrindylidene-2-acetone (compare Kon, J., 1926, 1792).—The ketone (15 g.) was added to "molecular" Na (2 g.) under dry Et₂O; after the reaction had abated an excess of MeI was introduced, and the whole refluxed on the steam-bath for 3 hrs. The filtered, washed (H₂O, dil. H₂SO₄, and H₂O), and dried liquid was distilled, leaving a considerable residue and giving fractions (i) 3.5 g., b. p. 131—138°/11 mm., (ii) 2.8 g., b. p. 139—143°/11 mm., and (iii) 2 g., b. p. 143—147°/11 mm.

The semicarbazone (m. p. 185—200°) from (i) was crystallised from EtOH. The solution deposited crystals, m. p. 160—180°, and the residue (m. p. 213°) was again boiled with EtOH, giving crystals, m. p. 218—220° (with considerable shrinking from 208°) (Found: C, 66.9; H, 9.0. C₁₄H₂₂ON₃ requires C, 67.4; H, 9.3%. C₁₃H₂₁ON₃ requires C, 66.4; H, 8.9%).

The semicarbazone (m. p. 203—206°) from (ii) was crystallised from abs. EtOH; m. p. 212° after shrinking.

The semicarbazone (m. p. 198—203°) from (iii) when crystallised from abs. EtOH, melted at 213—214°, leaving a residue, m. p. 210° (Found: C, 67.2; H, 9.0%).

The ketone regenerated from the sparingly sol. semicarbazone (4 g.) from all the above fractions by steam-distillation with dil. H_2SO_4 had b. p. 145—146°/11 mm., d_4^{20} 0.9770, n_D^{20} 1.5092, and J 4.7% (10 mins.).

In another experiment, *trans*-hexahydrohydrindylidene-2-acetone (10 g.), when similarly methylated, gave two fractions: (i) 2.4 g., b. p. 130—140°/10 mm., (ii) 2.2 g., b. p. 140°/10 mm. The semicarbazone (m. p. 185—195°) from (i) was crystallised from MeOH. The residue melted at 206—208°, and from the solution two crops were obtained after 20 mins. and 24 hrs. After a few crystals, the second crop crystallised from MeOH in flat needles or elongated plates, m. p. 175—177° (Found: C, 67.2; H, 9.4. $C_{14}H_{23}ON_3$ requires C, 67.4; H, 9.3%). The semicarbazone (m. p. 198°) from (ii) crystallised from MeOH in cubes, m. p. 206—208°, and only a very small quantity of the low-melting semicarbazone could be obtained from it.

The semicarbazone (0.75 g.), m. p. (170—175°) was shaken with $N/2-H_2SO_4$ and light petroleum (b. p. 40—60°) for 2 weeks (Kon, J., 1930, 1616). As most of it remained unhydrolysed, the ketone was regenerated with an excess of oxalic acid by steam-distillation. It had b. p. 138°/10 mm., n_D^{18} 1.4879, J 81.2% (10 mins.), and an odour quite distinct from that of the $\alpha\beta$ -ketone (XI).

Ethylation of trans-Hexahydrohydrindylidene-2-acetone.—This was done in the same way as the methylation. The orange colour of the solution did not disappear, as it did in the methylation. After refluxing for 8 hrs., the ethylated product (from 11 g. of the ketone) was steam-distilled and converted into the semicarbazone (1.4 g., m. p. 180—196°), which was boiled with MeOH. The readily sol. part separated in gritty crystals, m. p. 153° (Found: C, 68.1; H, 9.3. $C_{15}H_{25}ON_3$ requires C, 68.4; H, 9.6%), and 135—140° when mixed with the α -methyl- $\beta\gamma$ (?)-semicarbazone (m. p. 167—172°). The sparingly sol. part, m. p. 215°, had m. p. 225° after further crystals. (Found: C, 67.0; H, 9.1%), and did not depress the m. p. (222°) of the semicarbazone of the original ketone.

The ketone obtained from the residue in the steam-distillation flask had b. p. 147°/10 mm. and gave a semicarbazone, m. p. 152—158° after crystals from MeOH.

Equilibrations.—*trans*-Hexahydrohydrindylidene-2-acetone (6.25 g.) was treated with *N*-alc. NaOEt under Kon and Linstead's conditions. After 5 mins. treatment, the ketone had b. p. 142—144°/9 mm., d_4^{20} 0.9854, n_D^{20} 1.5120, and J 2.8% (10 mins.); after 1 hr. it had b. p. 143—144°/9 mm., d_4^{20} 0.9848, n_D^{20} 1.5120, and J 2.8%.

A few drops of the $\beta\gamma$ (?)-ketone, obtained from the lower-melting methylated semicarbazone, were treated with a large excess of NaOEt. The product gave a semicarbazone, m. p. 176—180° after crystals from MeOH, which did not depress the m. p. of the semicarbazone of the original $\beta\gamma$ (?)-ketone.

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