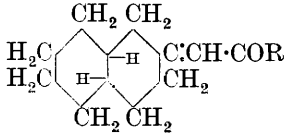
298. *Three-carbon Tautomerism in Dicyclic Systems. Part II. The Effect of an α-Methyl Group on Tautomerism in* trans-*β-Decalin Compounds.*

By R. S. Thakur.

This work was undertaken with the object of determining the effect of an α-methyl group on the mobility and equilibrium in the system (I), which contains a strainless ring, and of drawing a further analogy between the corresponding derivatives of *trans*-β-decalin and *cyclo*hexane.

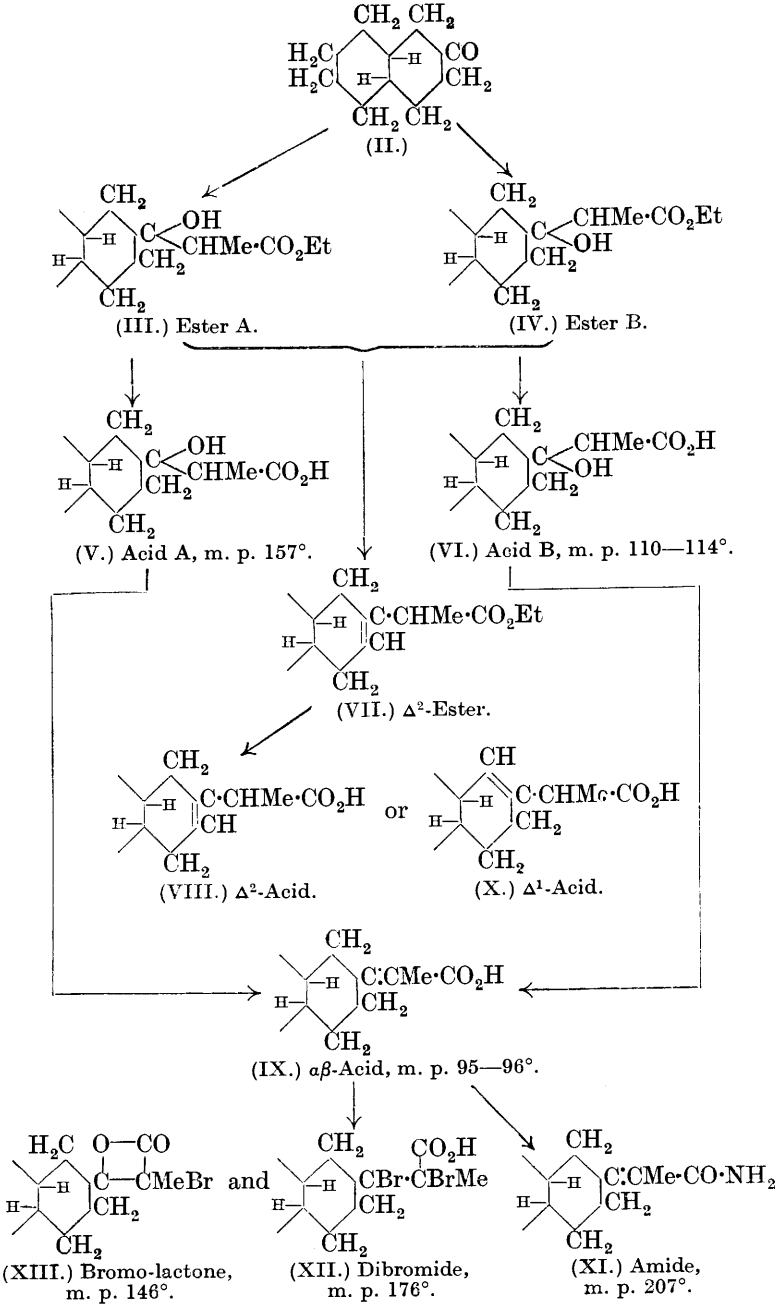
(I.) 

(R = OH, OEt, or Me)

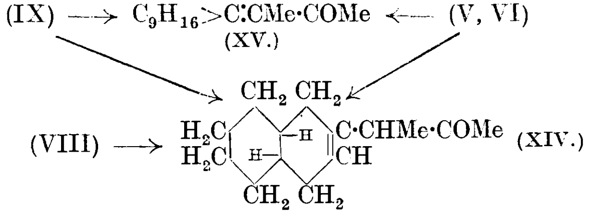
As already observed in the lower homologues (preceding paper), the compounds now obtained display the stereoisomerism which is to be expected: *e.g.*, the *hydroxy-ester* (from the condensation product of *trans*-β-decalone with ethyl α-bromopropionate in presence of zinc) is a mixture of two compounds (III and IV), which, though not isolated in a pure state, have different physical properties and give rise to two acids. The two *hydroxy-acids* A (V) and B (VI) differ in solubility in hot petroleum and benzene and can be obtained in quantity by careful fractional crystallisation. The acid A is less easily dehydrated than the acid B. Similarly, the dehydration of the hydroxy-ester was incomplete when phosphorus oxychloride was employed: the method of Darzens (*Compt. rend.*, 1911, **152**, 1601) was, however, satisfactory. The constitution of the αβ-acid (IX) was confirmed by its oxidation to *trans*-β-decalone (II). In the preparation of its *dibromo*-derivative (XII) by the addition of bromine to a chloroform solution of the αβ-acid, the *bromo-lactone* (XIII) was also obtained in good yield.

Oxidation of the βγ-ester gave *trans-cyclo*hexane-1 : 2-diacetic acid, which could result from the Δ^2-acid but not from the Δ^1-acid (X). Hence, as in the unsubstituted acid, the βγ-acid has the formula (VIII).

The βγ-*ester* was obtained by the method of partial esterification of the βγ-acid (Sudborough and Thomas, J., 1911, 99, 2307; Eccott and Linstead, J., 1929, 2153). The rate of esterification was very slow, as in the α-methyl*cyclo*hexenylacetic acid. The αβ-*ester* was prepared from the silver salt of the αβ-acid, and also by refluxing the acid with 4% alcoholic hydrogen chloride.


(II.)
(III.) Ester A.
(IV.) Ester B.
(V.) Acid A, m. p. 157°.
(VI.) Acid B, m. p. 110—114°.
(VII.) Δ²-Ester.
(VIII.) Δ²-Acid.
or
(X.) Δ¹-Acid.
(IX.) αβ-Acid, m. p. 95—96°.
(XIII.) Bromo-lactone, m. p. 146°.
and
(XII.) Dibromide, m. p. 176°.
(XI.) Amide, m. p. 207°.

α-Methyl-Δ^2-trans*-octahydronaphthyl-2-acetone* (XIV) could be readily prepared either by direct synthesis from the βγ-acid (VIII) or by the methylation of Δ^2-*trans*-octahydronaphthyl-2-acetone (70% yield) (compare Kon. J., 1926, 1792). The synthesis of α-methyl-*trans*-decahydronaphthylidene-2-acetone (XV), however, presented great difficulties owing to the considerable conversion of the αβ-acid chloride into the βγ-isomeride on distillation. Only a small quantity of its *semicarbazone* was obtained from the undistilled αβ-acid chloride and methylzinc iodide. Similar treatment of the distilled chloride from the hydroxy-acid gave a mixture of the αβ- and the βγ-ketone, the latter preponderating (compare Kon and Narayanan, J., 1927, 1546).



Tautomerism of the Acids, Esters, and Ketones.

Acids.—The point of equilibrium and the mobility of this pair of acids (VIII, IX) could not be determined on account of experimental difficulties.

Esters.—Some equilibrations were carried out under Kon and Linstead's conditions (J., 1929, 1269), but the change was surprisingly slow—16% in 36 days. Similarly, mixtures of the αβ- and the βγ-ester did not undergo sufficient change under these conditions. At the temperature of the steam-bath, however, there was no undue amount of hydrolysis and the recovery of the esters was good. The αβ-ester takes a little more than 6 hours to reach equilibrium, and the βγ- less than 3 hours. The mobility is 0·06 and the point of equilibrium about 10% αβ.

Ketones.—The mobility of the ketones (XIV) and (XV) could not be determined on account of the scarcity of the αβ-isomeride; the equilibrium is almost completely on the βγ-side, since no appreciable change in its iodine addition or physical properties could be observed on equilibrating the βγ-ketone (XV).

These results are tabulated in Parts I and IV (pp. 2127, 2160).

With the exception, possibly, of the ketones, it can thus be concluded that the α-methyl group has a very great retarding effect on the tautomeric mobility of the unsaturated acids and esters of the *trans*-β-decalin series. The point of equilibrium in the esters and ketones is also shifted to the βγ-side and there is thus a close agreement between the values of equilibrium of the corresponding compounds of *trans*-β-decalin and *cyclo*hexane.

EXPERIMENTAL.

Acids.

Condensation of trans-*β-Decalone with Ethyl α-Bromopropionate. Ethyl 2-Hydroxy*-trans-*decalin-2-α-propionate.*—*trans*-β-Decalone (304 g.), ethyl α-bromopropionate (252 c.c.), and Zn (135 g.) in C_6H_6 (800 c.c.) reacted vigorously on the steam-bath. The main quantity of the *hydroxy-ester* had b. p. 178—180°/10 mm. (there was some lower fraction, b. p. 140—176°/10 mm.). On redistillation 15 g. of the main ester gave 2 g., b. p. 150—171°/9 mm., $d_{4^\circ}^{19\cdot9^\circ}$ 1·0227, $n_D^{19\cdot9^\circ}$ 1·4811, $[R_L]_D$ 70·74, and the rest boiled at 170—172°/9 mm. and had $d_{4^\circ}^{18\cdot3^\circ}$ 1·0286, $n_D^{19\cdot8^\circ}$ 1·48205, $[R_L]_D$ 70·24 (calc., 70·25) (Found: C, 70·7; H, 10·1. $C_{15}H_{26}O_3$ requires C, 70·9; H, 10·2%). The total yield of the ester (calculated from the hydroxy-acid) was 76%; uncondensed decalone (b. p. 112—114°/11 mm.) 13%; self-condensation product of decalone 7%.

Hydrolysis of the Hydroxy-ester. Stereoisomeric 2-Hydroxy-trans-*decalin-2-α-propionic Acids.*—The lower-boiling ester (140—176°/10 mm.) was hydrolysed for 18 hrs. with 10% aq. methyl-alcoholic NaOH at room temp. The alcohol was distilled off in vac. below 40°, the residue diluted with H_2O, the unhydrolysed matter extracted with ether, and the alkaline solution acidified. The acids were taken up in Et_2O and recovered as a hard solid, which was crystallised from C_6H_6–petroleum (b. p. 60—80°). The less sol. *acid A* was very sparingly sol. in C_6H_6 and separated immediately from a hot solution (when mixed with the acid B, it only crystallised slowly after addition of light petroleum); m. p. 156—157° (Found: C, 69·2; H, 9·7; equiv., by titration, 226·1. $C_{13}H_{22}O_3$ requires C, 69·0; H, 9·7%; equiv., 226·2).

The more sol. *acid B* was obtained in colourless crystals, m. p. 102—104°, when the C_6H_6–petroleum mother-liquor was cooled in ice. It was fairly readily sol. in light petroleum (b. p. 60—80°), from which it crystallised in clusters of prismatic needles, m. p. 110—114° (Found: C, 68·8; H, 9·6%; equiv., 225·6).

The acid obtained from the hydrolysis of the bulk of the hydroxy-ester, b. p. 178—180°/10 mm., was also separated by fractional crystallisation into the two forms A and B; that obtained from the undistilled ester left in the flask crystallised from C_6H_6–petroleum in radiating needles, m. p. 154—156°. The neutral substance from the last hydrolysis was Δ^2-*trans*-octahydronaphthyl-2-β-decalone (see preceding paper).

Dehydration of the Hydroxy-ester.—As the use of $POCl_3$ gave an unsatisfactory result, thionyl chloride (30 g.) was added drop-wise to a mixture of the hydroxy-ester (mixture of III and IV: 64 g.) and pyridine (40 g.) at 0°. The pale yellow product was left overnight at room temp. and then worked up as described on p. 2131; the dehydrated ester (57 g.; 96% yield) had b. p. 156—158°/10 mm.; $d_{4^\circ}^{19\cdot8^\circ}$ 0·9895, $n_D^{19\cdot9^\circ}$ 1·4841, whence $[R_L]_D$ 68·52 (calc., 68·26); *J* 36·7% (10 mins.), 47·6% (30 mins.), 53·7% (60 mins.).

Δ^2-*Octahydronaphthalene-2-α-propionic Acid* (VIII).—The above ester was hydrolysed with cold 10% aq.-alc. NaOH for 24 hrs. and the resulting liquid acid was repeatedly partially esterified to ensure that there was no αβ-isomeride. The pure βγ-ester gave on hydrolysis a liquid *acid* which distilled as a colourless liquid like glycerol, b. p. 186°/13 mm. (slight decomp.), 148—149°/*ca.* 1 mm., *J* 89% (Found: C, 74·6; H, 9·5; equiv., by titration, 207·8. $C_{13}H_{20}O_2$

requires C, 74·9; H, 9·7%; equiv., 208·2). It absorbed Br very readily in $CHCl_3$, giving a sticky bromo-derivative.

The *amide*, prepared from the acid chloride (b. p. 155—156°/17 mm.) and dry NH_3 in cold Et_2O, was very sol. in C_6H_6 and crystallised from C_6H_6–petroleum (b. p. 60—80°) in clusters of colourless needles, m. p. 133—134° after sintering (Found: C, 75·4; H, 10·1. $C_{13}H_{21}ON$ requires C, 75·3; H, 10·2%).

Dehydration of the Hydroxy-acid with Acetic Anhydride.—The crude acid (60 g.; mixture of A and B) was refluxed with Ac_2O (80 c.c.) for 3 hrs., H_2O added, the excess of Ac_2O removed under reduced press., the residue extracted with Et_2O, and the solvent removed wet. The product was treated with hot Na_2CO_3 aq., which left a small quantity of a sweet-smelling oil and extracted a viscous acid (50 g.): steam-distillation of this gave 0·05 g. of a solid acid, which served to solidify the bulk of the acid. trans-*Decahydronaphthylidene*-2-*a*-*propionic acid* (IX) separated slowly from light petroleum (b. p. 60—80°) in well-formed crystals, m. p. 95—96° (Found: C, 74·7; H, 9·4; equiv., 207·7. $C_{13}H_{20}O_2$ requires C, 74·9; H, 9·7%; equiv., 208·2).

A search was made for the second isomeride of the $\alpha\beta$-acid. The petroleum mother-liquor gave a little more solid $\alpha\beta$-acid on evaporation, but the rest was a thick liquid. Some of this was partially esterified, the unesterified acid, which still would not solidify, was converted through its silver salt into the ethyl ester, which was fractionally distilled: (i) b. p. 171—177°/20 mm., $d_{4°}^{20\cdot2°}$ 1·0008, $n_{D}^{20\cdot2°}$ 1·4912, J 6·7% (60 mins.); (ii) b. p. 177—185°/20 mm., $d_{4°}^{20\cdot2°}$ 1·0118, $n_{D}^{20\cdot2°}$ 1·4872, J 2·5% (60 mins.). On hydrolysis, the latter gave a semi-solid acid, which was triturated with light petroleum. The colourless solid acid which separated was insol. in hot petroleum (b. p. 60—80°), crystallised from benzene (m. p. 154—155°), and was identified as the hydroxy-acid A (V).

The rest of the liquid acid from the petroleum mother-liquor was further dehydrated with Ac_2O (4 hrs.), and the resulting acid partially esterified for 65 hrs. The unesterified acid yielded some more solid $\alpha\beta$-acid, whereas the higher fraction of the ester [(i) b. p. 160—166°/19 mm.; (ii) 168—183°/19 mm.] still indicated the presence of the hydroxy-acid.

The acid (m. p. 95—96°) was oxidised with 3% $KMnO_4$ aq. in cold $NaHCO_3$ aq. The *trans*-β-decalone (b. p. 112°/14 mm.) produced was identified by its characteristic odour and semicarbazone (m. p. and mixed m. p. 192—193°).

The *amide* (XI), prepared from the undistilled acid chloride and dry NH_3 in Et_2O, was sparingly sol. in C_6H_6 and crystallised from it in clusters of colourless hairy needles, m. p. 206—207° (Found: C, 75·1; H, 10·1. $C_{13}H_{21}ON$ requires C, 75·3; H, 10·2%).

Bromine (0·73 c.c.) in $CHCl_3$ was added to a $CHCl_3$ solution of the $\alpha\beta$-acid (3 g.). After 24 hrs., the solvent was distilled in vac. and the residue triturated with light petroleum (b. p. 60—80°). The *dibromide* (XII) crystallised from C_6H_6–petroleum (b. p. 60—80°) in gritty masses, m. p. 175—176° (violent decomp.) (Found: C, 42·2; H, 5·3. $C_{13}H_{20}O_2Br_2$ requires C, 42·4; H, 5·5%).

The benzene–petroleum mother-liquor gave two more crops of crystals on standing. These crystallised from C_6H_6–petroleum in spindle-like clusters of soft needles of the *bromo-lactone* (XIII),* m. p. 145—146° (violent decomp.) (Found: C, 54·0; H, 6·5. $C_{13}H_{19}O_2Br$ requires C, 54·3; H, 6·7%).

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* (*Added in proof*). This compound is probably the unsaturated bromo-acid, $C_9H_{15}{\gg}C\cdot CMeBr\cdot CO_2H$, as it dissolves in cold $NaHCO_3$ aq. and dil. NH_3 aq. and decolorises $KMnO_4$ aq. It does not, however, add on Br_2.

Reference Curve.—The iodine additions (J) of the acids and their mixtures were determined by Linstead and May's method, following the modifications described in the preceding paper (p. 2132). The solution of the $\beta\gamma$-acid was slightly turbid.

A reference curve was plotted from the following values :

% $\alpha\beta$ ...	0	10	20	30	40	50	60	75	90	100
J, % ...	93·1	84·5	76·9	68·5	59·5	50·2	40·8	26	10·7	0·4

Equilibrations.—The $\alpha\beta$-, $\beta\gamma$-acids and their mixtures were boiled with KOH aq. with the following results :

TABLE 1.

Acid.	KOH, %.	Time.	J, %.	Comp., % $\alpha\beta$.
$\alpha\beta$	[10] × 17	232 hrs.	5	96
$\alpha\beta$	[10] × 17	72 days	13·4	87·5
$\alpha\beta$	[30] × 35	23 days	27	74
$\beta\gamma$	[10] × 17	232 hrs.	90·7	3
$\beta\gamma$	[10] × 17	72 days	88	6
60% $\beta\gamma$ 40% $\alpha\beta$	[13] × 18	60 days	62·2	37
70% $\beta\gamma$ 30% $\alpha\beta$	[12] × 16	60 days	70·5	27·5
80% $\beta\gamma$ 20% $\alpha\beta$	[12] × 17	60 days	78·3	18

Lower concentrations of the alkali were used because the potassium salts of the acids dissolved in them at the b. p. As seen from the last column, it was not possible to determine the point of equilibrium on account of the change being extraordinarily slow.

Esters.

Preparation of Ethyl trans-*Decahydronaphthylidene*-2-α-*propionate.*—(i) *Through the silver salt.* The $\alpha\beta$-acid dissolved readily in NH_3 aq. On removal of the excess of NH_3, the solution became gelatinous or colloidal but cleared again on addition of a drop of the reagent. The Ag salts are readily dried if they are finally washed with some light petroleum. The *ester* was a colourless liquid with no unpleasant smell; b. p. 169°/16 mm.; $d_{4^\circ}^{20^\circ}$ 0·9918, $n_D^{20^\circ}$ 1·4969, whence $[R_L]_D$ 69·68 (calc., 69·26); J 1·2% (60 mins.), 1·6% (90 mins.). The lower value of the exaltation (0·42) on account of branched conjugation is noteworthy (in the unsubstituted esters, it is 1·58) (Found : C, 76·1; H, 10·0. $C_{15}H_{24}O_2$ requires C, 76·3; H, 10·2%). The ester gave decalone (b. p. 112°/14 mm.; semicarbazone, m. p. and mixed m. p. 192—193°) on ozonisation in $CHCl_3$ at 0°.

(ii) *By alcoholic hydrogen chloride.* The $\alpha\beta$-acid (26 g.) and 4% alc. HCl (75 c.c.) were refluxed on the steam-bath for 10 hrs. 8 G. of the acid were recovered, and the ester (16 g.) had b. p. 172—173°/19 mm., $d_{4^\circ}^{20^\circ}$ 0·9901, $n_D^{20^\circ}$ 1·4968, and J 4·4% (60 mins.).

Ethyl Δ^2-trans-*Octahydronaphthalene*-2-α-*propionate.*—The physical properties of the *ester* obtained by repeated partial esterifications of the $\beta\gamma$-acid for short periods (17—24 hrs.) did not vary and were b. p. 163—164°/19—20 mm.; $d_{4^\circ}^{17\cdot6^\circ}$ 0·9831, $n_D^{20^\circ}$ 1·4821, whence $[R_L]_D$ 68·45 (calc., 68·26); J 65% (Found : C, 76·0; H, 10·0. $C_{15}H_{24}O_2$ requires C, 76·3; H, 10·2%).

Ozonisation of the $\beta\gamma$-Ester.—Ozonised oxygen was passed through a $CHCl_3$

solution of the pure $\beta\gamma$-ester (11 g., b. p. 159—160°/17 mm.), the solvent removed in vac., the product subjected to steam-distillation, and the residue treated with Na_2CO_3 aq. After being shaken with Et_2O, the alkaline solution on acidification gave an acid, which slowly partly solidified. The solid, m. p. 165°, was identified as *trans-cyclo*hexane-1 : 2-diacetic acid. The liquid portion, oxidised with 3% $KMnO_4$ aq. in cold $NaHCO_3$ aq., gave a product, which also partly solidified. Trituration with cold C_6H_6 left *trans-cyclo*hexane-1 : 2-diacetic acid (m. p. and mixed m. p. 167°) and removed a ketone which reacted with semicarbazide acetate to give the *semicarbazone* of *trans-cyclo*hexane-1-acetic acid-2-methyl ethyl ketone, elongated prismatic plates, m. p. 203° (decomp.), from abs. EtOH (Found: C, 57·5, 57·7*; H, 8·7. 8·4*; N, 15·2, 15·2*. $C_{13}H_{23}O_3N_3$ requires C, 58·0; H, 8·6; N, 15·6%).

Reference Curve.—The values of *J* for the same sample of $\beta\gamma$-ester varied slightly at different times. Hence, in order to minimise the error, the reference curve data were found at the time of the iodometric analysis of the equilibrated esters.

% $\alpha\beta$ ...	0	10	20	30	40	50	60	75	90	100
J, % ...	67·5	63	58·4	53·6	47·8	41·9	35·1	24·4	10·9	1·4

Equilibrations.—All the experiments were carried out with the theoretical quantity of *N*-NaOEt prepared in specially dried EtOH. As the change was slow at 25°, some experiments were carried out on the steam-bath. The results are in Table II.

TABLE II.

Expt.	Ester.	Temp.	Time, hrs.	Re-covered, %.	B. p./mm.	$n_D^{t°}$.	*J*, %.	% $\alpha\beta$.
1	$\alpha\beta$	25°	480	76	169—170°/19	1·4935/22·7°	13·4	87
2	,,	,,	856	66	168/18	1·4930/20·6	16·2	84
3	,,	100	3	71	161—168/22	1·4856/22·3	49·8	37
4	,,	,,	6		164—167/22	1·4837/22·3	55	27·5
5	,,	,,	12		165—166/21	1·4825/22·3	59·9	17
6	,,	,,	22	76	162—164/18	1·4825/20·2	61·6	13
7	$\beta\gamma$	,,	3		166/22	1·4821	61·6	13
8	,,	,,	6		162—164/21	1·4824	61·4	13·5
9	,,	,,	12		162—163/21	1·4824	60·9	15
10	,,	100	22		163—164/18	1·4837	61·6	13
11	90% $\beta\gamma$ 10% $\alpha\beta$	20	856	55	163—165/18	1·4860	60·9	14·5
12	80% $\beta\gamma$ 20% $\alpha\beta$	,,	,,	48	163/17—18	1·4872	58·2	20·5
13	70% $\beta\gamma$ 30% $\alpha\beta$	,,	,,	49	163—165/18	1·4887	54·4	29

The acid resulting from the hydrolysis of the esters was collected and analysed iodometrically.

Acid from	% Recovered.	Comp., % $\beta\gamma$.
Expts. 2, 3 and 4	20	83
Expts. 7—10	14	95
Expts. 11—13 and 2	30	86

The rate of hydrolysis of the two esters seems to be of the same order as their proportion in the equilibrium mixture (compare Kon and Linstead, *loc. cit.*).

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* Analyses by Dr. Ing. A. Schoeller.

There was no appreciable formation of the ethoxy-ester, as the undistilled residue accumulated from experiments 11—13 (36 days) had b. p. 165°/18 mm. and *J* 50·9% (35% *αβ*). Moreover the equilibrated *αβ*- and *βγ*-esters were analysed [Found for the *βγ*-ester (12 hrs.) : C, 75·9; H, 10·2. Found for the *αβ*-ester (12 hours) : C, 75·9; H, 10·2. $C_{15}H_{24}O_2$ requires C, 76·3; H, 10·2%. The ethoxy-ester, $C_{17}H_{30}O_3$, requires C, 72·3; H, 10·6%].

From the table, 13% *αβ* : 87% *βγ* seems to be the ratio at equilibrium, but the more accurate figure will probably be 10% *αβ*. The mobility calc. from experiments (1) and (2) is of the order 0·058, *i.e.*, nearly a hundredth that of the unsubstituted esters.

Ketones.

*Semicarbazone of α-Methyl-*trans*-decahydronaphthylidene-2-acetone.*—The *αβ*-acid (IX) (9 g.) and thionyl chloride (6 c.c.) were kept together at room temp. till all the acid had disappeared; the mixture was then warmed at 35° for a few mins., and the excess of the reagent removed under reduced pressure. The residue was diluted with dry Et_2O and treated with ZnMeI at − 40° (Blaise and Maire, *Ann. Chim. Phys.*, 1908, **15**, 556; Dickins, Hugh, and Kon, J., 1928, 1630). As the addition of H_2O to the filtered ethereal solution produces a slimy mixture, it is best to wash it first with sat. $(NH_4)_2SO_4$ aq. The solvent was distilled at a low temp., and the residue treated with semicarbazide acetate. The *semicarbazone*, m. p. 196—197° without purification, crystallised from C_6H_6 or MeOH in clusters of silky needles, m. p. 209—210° (Found : C, 68·2; H, 9·3. $C_{15}H_{25}ON_3$ requires C, 68·4; H, 9·5%). It depressed the m. p. of the *βγ*-semicarbazone, m. p. 195—196° (mixed m. p. 170—176°).

The distilled acid chloride of the *αβ*-acid gave on treatment with hot 10% Na_2CO_3 aq. an acid with *J* 66·4% (67·5% *βγ*), whereas the undistilled acid chloride gave an acid with *J* 14% (13·5% *βγ*). In all these decompositions, a considerable quantity of a neutral residue was left which was probably the anhydride.

*Semicarbazone of α-Methyl-Δ²-*trans*-octahydronaphthyl-2-acetone.*—(i) *From the βγ-acid.* The acid (28 g.) was converted into the acid chloride (b. p. 159—161°/19 mm.; 26 g.) with thionyl chloride (15 c.c.). On treatment with ZnMeI, the ketonic product (b. p. 154—156°/19 mm.; 16 g.) readily gave the pure *semicarbazone*, m. p. 194° without any purification. It crystallised from C_6H_6 in minute crystals and from MeOH in rhomboid plates on long standing (Found : C, 68·1; H, 9·5. $C_{15}H_{25}ON_3$ requires C, 68·4; H, 9·5%). The *ketone* produced from it with oxalic acid had b. p. 153—154°/19 mm.; $d_{4°}^{22°}$ 0·9574, $n_D^{22°}$ 1·4912, whence $[R_L]_D$ 62·38 (calc., 62·13); *J* 78% (Found : C, 81·2; H, 10·5. $C_{14}H_{22}O$ requires C, 81·5; H, 10·7%).

(ii) *From the hydroxy-acid* (compare Kon and Narayanan, *loc. cit.*). The acid chloride (16 g., from 23 g. of acid and 20 c.c. of thionyl chloride) was a colourless mobile liquid, b. p. 161—162°/20 mm. The ketonic product (9 g., b. p. 155—156°/20 mm.) from the Blaise–Maire reaction readily gave a semicarbazone, m. p. 193—194°, and 194—195° after crystn. from C_6H_6, identical with the *βγ*-semicarbazone. A small quantity of the *αβ*-semicarbazone, m. p. 202—203°, was isolated by fractional crystn. from some low-melting semicarbazone.

On treatment of the above acid chloride with hot Na_2CO_3 aq., the resulting acid had *J* 86%, corresponding to 91% *βγ*-acid.

(iii) *From the αβ-acid.* When the distilled acid chloride of the *αβ*-acid was used in the synthesis, the resulting ketone gave the *βγ*-semicarbazone, m. p. 192—194°, and 195—196° after crystn. from C_6H_6.

(iv) *By methylation of* Δ^2-trans-*octahydronaphthyl-2-acetone* (compare Kon, *loc. cit.*). The ketone (10·6 g., recovered from the equilibration experiments) was added to " molecular " Na (1·3 g.) covered with dry Et_2O. After the reaction had subsided, an excess of MeI was added to the orange-coloured liquid and the whole was refluxed for 4 hrs. On being worked up in the usual way, the distillate (7·5 g.; 70% yield) came over at 152—156°/17 mm. (original b. p. 146°/15 mm.) and yielded a colourless cryst. semicarbazone, m. p. 192—194°. It separated from C_6H_6 in minute crystals, m. p. 194—195°. The ketone regenerated from it with oxalic acid by steam distillation (the ketone is volatile in steam with difficulty) had b. p. 153—154°/19 mm., $d_{4°}^{21·7°}$ 0·9571, $n_D^{21·7°}$ 1·4910, $[R_L]_D$ 62·39 (calc., 62·13).

Equilibrations.—The pure ketone was left with an excess of *N*-NaOEt fo 15 hrs. at room temp. It was then recovered and had b. p. 154—155°/19 mm., $d_{4°}^{22·5°}$ 0·9570, $n_D^{22·5°}$ 1·4913, and *J* 77·2%. Another specimen was warmed with an excess of *N*-NaOEt on the steam-bath for 3 hrs. It boiled at 155°/19 mm. and had $d_{4°}^{22·5°}$ 0·9579, $n_D^{22·5°}$ 1·4918, and *J* 76·3%. Hence the position of equilibrium is almost on the side of pure $\beta\gamma$-ketone.

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