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JERVINE—XIII

C/D RING *CIS-TRANS* EQUILIBRIA IN TETRAHYDROJERVINE DERIVATIVES WITH OPEN RING E

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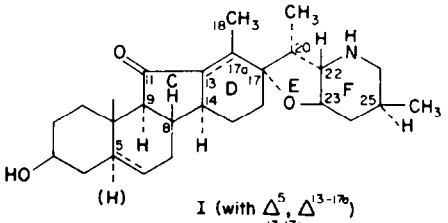
Abstract—The levorotatory acetolysis product IV of tetrahydrojervine (III) and the dextrorotatory isomer formed from it on treatment with alkali and reacetylation[4] have been recognized, respectively, as the C/D *cis*-linked 13α-epimer Va and the C/D *trans*-linked 13β-epimer VIa. In both compounds the 17a-methyl group is β-oriented.

In alkaline methanol–tetrahydrofuran solution at 22° equilibrium is reached with 81% of the C/D *trans*-compound present. Configurational assignments (C-13, C-17) have been made on the basis of similar equilibrium studies for the 16,17-dihydro derivative VIIa (C/D *cis*) formed in the catalytic reduction of Va,[4] and for the two dihydro products VIII and IXa (C/D *trans*) obtained in the same manner from VI.[4] The results of this study serve to illustrate again the importance of conformational factors for the position of the *cis–trans* equilibrium in Δ^5-hydrinden-1-one and hydrindan-1-one systems. They also allow to assign the α-configuration to the hydrogens at C-1 and C-17a in tetrahydrojervine (III).



I (with Δ^5, $\Delta^{13\text{-}17a}$)
II (no $\Delta^{13\text{-}17a}$)
III (no Δ^5, $\Delta^{13\text{-}17a}$)

THE configurations of carbon atoms 13 and 17a in 13,17a-dihydrojervine (II) and 5,6,13,17a-tetrahydrojervine (III), which are obtained from jervine (I) by catalytic reduction,[1] have not been determined as yet experimentally, although it has been suggested,[2] on the basis of the rear addition rule, that the hydrogen atoms in these positions are α-oriented.[3] The facts presented in the following shows that such is indeed the case. This conclusion is based on the behaviour towards strong alkali of certain derivatives of tetrahydrojervine in which rings D and F are no longer bridged by oxygen to form the tetrahydrofuran ring E, and some of which undergo partial

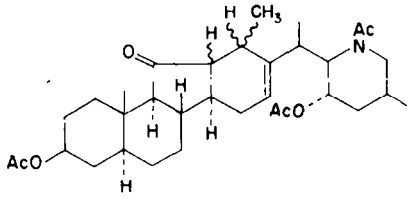
[1] W. A. Jacobs and C. F. Huebner, *J. Biol. Chem.* **170**, 635 (1947).

[2] B. M. Iselin, M. Moore and O. Wintersteiner, *J. Amer. Chem. Soc.* **78**, 403 (1956), Footnote 6.

[3] The configurations of all the other asymmetric carbon atoms have been established as those shown in I [for references see Footnote 4 in the paper XI of this series, *J. Org. Chem.* **29**, 262 (1964)] with the exception of the configurations of C-17 and C-20 which so far rest on biogenetic analogy only.[2]

[4] O. Wintersteiner, M. Moore and B. M. Iselin, *J. Amer. Chem. Soc.* **76**, 5609 (1954).

or nearly complete epimerization at carbon atom 13 under these conditions. As expected, the proportion of epimers at equilibrium is governed by the conformation of ring D and of the alkyl substituent at C-17a, and also that at C-17 when this carbon atom is asymmetric.



IV

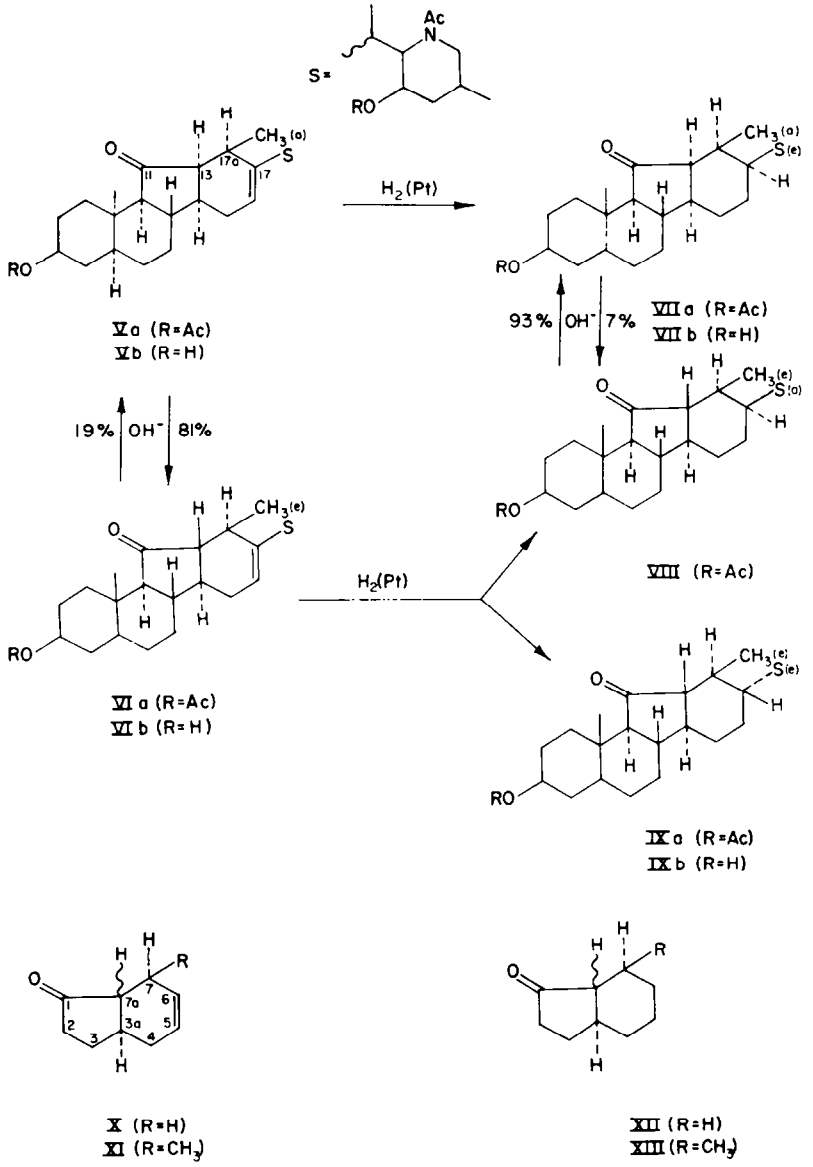
In 1954 we reported on an acetolysis product (m.p. 231°, $[\alpha]_D$ −72·5°) of 3,N-diacetyltetrahydrojervine which was shown to have the Δ^{16}-structure IV.[4] When this compound was O-deacetylated with boiling methanolic potassium hydroxide, it formed a *dextrorotatory* N-acetyl derivative (m.p. 229°, $[\alpha]_D$ +17°) which on re-acetylation gave a likewise dextrorotatory *iso*-triacetate (m.p. 191°, $[\alpha]_D$ +25°). Of the two explanations which suggested themselves for this isomerization, namely, epimerization at C-13 or double bond migration, slight preference was given at that time to the latter, mainly because the ketones obtained from the original triacetate and the iso-triacetate by allylic oxidation with chromium trioxide exhibited marked differences in their UV and IR spectra. We have now found that both isomers exhibit in their NMR spectra a signal for a vinylic proton (at $\tau = 4{\cdot}38$ and 4·42 respectively), and therefore differ from each other not by double bond isomerism but by epimerism at C-13.

Further study of the isomerization reaction and of the behaviour towards alkali of the 16,17-dihydro derivatives obtained from the two isomeric olefins has made it clear that the original acetolysis product must be the 13α-epimer V with rings C and D *cis*-linked, and the *iso*-compound the 13β-epimer VI, with C/D-*trans* junction.

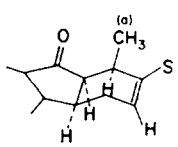
House and Rasmussen[5] have recently shown that while with hydrind-5-en-1-one (X) the ratio of *trans* to *cis* form after equilibration in triethylamine at 100° is 0·9 (47% *trans*), with the presence of a methyl group in position 7 *trans* to the 3a-hydrogen (XI)—precisely the situation obtaining in V and VI—the *trans*-form greatly preponderates (*trans*/*cis* > 50). We have followed the mutarotation at 22° of both the acetolysis product Va and of the *iso*-N-acetyl derivative VIb in 1:1 methanol–tetrahydrofuran containing 2% potassium hydroxide, and find that equilibrium is attained in a few hours at a rotation value corresponding to a ratio VIb/Vb of 4·27 (81% of VIa).[6] There can be hardly any doubt then that the acetolysis product Va is the C/D *cis*-linked, and the *iso*-compound VIa the C/D *trans*-linked, isomer.

[5] H. O. House and G. A. Rasmussen, *J. Org. Chem.* **28**, 31 (1963).

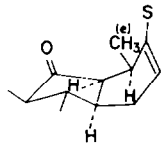
[6] Since V was present in the equilibrium mixture not as the starting triacetate Va but as the N-acetyl derivative Vb—which we were unable to obtain in pure form either from the mother liquors of the *iso*-N-acetyl derivative VIa or by acid-catalyzed hydrolysis of the triacetate Va,—it had to be assumed, in calculating the position of the equilibrium from the rotation data, that the molecular rotation change accompanying the O-deacetylation of Va was negligible in comparison with the mutarotation change. For discussion of this point and of the mode of calculation see the experimental section.



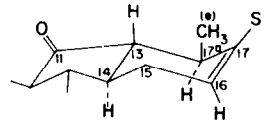
The 16,17-double bond of both the acetolysis product Va and the *iso*-triacetate VIa could be readily reduced catalytically.[4] From Va there was thus obtained as the *sole product* a levorotatory dihydro derivative (m.p. 243°, $[\alpha]_D$ −39°), now formulated for the reasons given below as the 13α-isomer with the 17-side chain S in the β-configuration (VIIa). The N-acetyl derivative VIIb obtained from VIIa by O-deacetylation with alkali (m.p. 218°, $[\alpha]_D$ −46°) reverted to VIIa on acetylation,[4] and hence VII must represent the stable 13-epimer. On the other hand, the catalytic reduction of the *iso*-triacetate VIa afforded *two* dihydro derivatives separable by chromatography, a crystalline compound (m.p. 225°, $[\alpha]_D$ −18·5°) and an amorphous product ($[\alpha]_D$ −14°) which, however, showed the expected analytical composition.[4]



V-A



V-B



VI

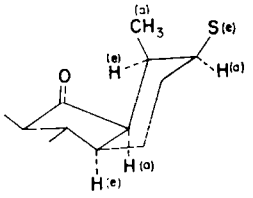
The crystalline triacetate m.p. 225° could also be obtained in low yield by hydrogenating the *iso*-N-acetyl derivative VIb and acetylating the resulting amorphous product, which was not further characterized.[4]

These two C/D *trans*-dihydro compounds, which obviously differ by epimerism at C-17, have now been subjected to saponification with alkali. The crystalline triacetate m.p. 225° was thereby almost quantitatively converted to the C/D *cis*-dihydro N-acetyl derivative VIIb, a result confirmed by the equilibration experiment at 22° which indicated a *cis-trans* ratio at equilibrium of about 14 (93% *cis*). The other, amorphous triacetate yielded under the same conditions a crystalline N-acetyl derivative m.p. 241°, $[\alpha]_D$ −14°, which on reacetylation gave back the amorphous starting product with $[\alpha]_D$ −18·7°. As will be made clear below, the crystalline triacetate m.p. 225° which suffers inversion at C-13 with alkali must be the epimer with the 17-side chain β-oriented (VIII), and hence the amorphous, not epimerizable triacetate its 17-epimer with the side chain in the α-configuration.

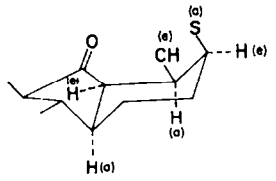
With the help of scale models (Dreiding-Stereomodels) the facts presented above can be rationalized as follows:

The C/D *cis*-linked olefin Va can exist in two forms, A and B, in both of which ring D is a somewhat distorted boat, as House and Rasmussen[5] postulate also for the simple hydrindenones X and XI. Aside from the element of energetic instability inherent in the boat conformation, the 17a-methyl group must be, in the light of the findings of these authors, a factor contributing to this instability, in A by its axial character which brings it into close proximity to the 19-methyl group, and in B, where it is equatorial, by 1,3-interaction with the 11-carbonyl oxygen. Moreover, in B there is the unfavorable general crowding of the space above the C/D ring junction caused by the pronounced upward tilt of ring D with its bulky S-substituent. In contrast, the C/D moiety of the *trans* isomer VI is essentially flat, and, with the 17a-methyl group being equatorial, devoid of unfavorable steric interactions.

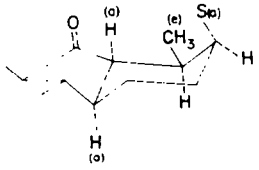
It is also clear from the spatial characteristics of the two forms of V just outlined that catalyst approach in the catalytic reduction of the double bond could occur only from the rear, and hence only one dihydro product would be formed, as is actually the case. The 17-side chain in this dihydro isomer must therefore be β-oriented. The stereochemistry of this isomer could then be either that depicted in VII-A, in which the 17-substituent is equatorial and the 17a-methyl group axial, or that of VII-B, in which these conformations are reversed. In view of the fact that VII is essentially stable to alkali, form A seems much more likely, since it stands to reason that the stabilizing influence of the large side chain substituent at C-17, when in the equatorial conformation as in VII-A, would by far outweigh the destabilizing effect of the axial methyl group on the neighboring carbon atom. A corollary of this assumption is that when the 17-side chain is axial, it will tend to become equatorial by forcing, in the presence of alkali, the inversion of carbon atom 13.



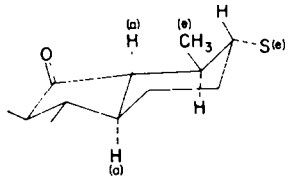
VII - A



VII - B



VIII



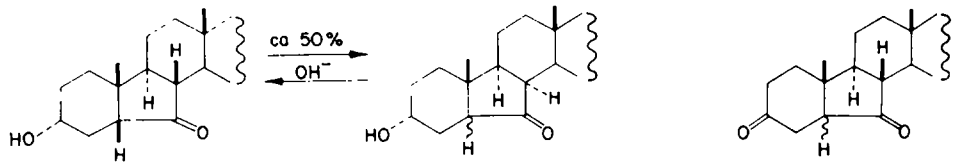
IX

That the conformation of the 17-substituent is indeed of overwhelming importance in determining the configuration of C-13 in the hydrindan-1-one system of these dihydro compounds follows from the behavior towards alkali of the two 17-epimeric dihydro products derived from the C/D *trans*-fused olefin VI. The steric characteristics of VI mentioned further above explain why two isomers are formed: catalyst approach is possible from both faces of ring D. If it is from the α-side, isomer VIII, in which the 17-substituent is β and axial, is formed, and this should be the crystalline compound m.p. 225° which on treatment with alkali yields the C/D *cis* dihydro compound VII having this substituent in the equatorial conformation, even though the 17a-methyl group, which is equatorial in VIII, becomes axial in this change. Hydrogen addition from the β-side, on the other hand, produces the isomer IX in which the 17-substituent is α, and equatorial, as is the 17a-methyl group, and hence this isomer does not epimerize at all at C-13 with alkali. It should be noted that in the comparable indanone XIII[5] in which the 7-methyl group is the only conformational factor influencing the *trans*/*cis* ratio characteristic for the system lacking this methyl substituent (XII, *trans*/*cis* = 0·33), this influence favours the *trans*-isomer (*trans*/*cis* = 3·08). It is clear from the *trans*/*cis* ratio = 0·072 in the equilibrium VII ⇄ VIII that the β-oriented side chain at C-17 almost completely extinguishes this effect of the methyl group. On the other hand, the α-oriented side chain in IX, working in the same direction as the methyl group, effects complete stabilization of the *trans* ring junction. These results demonstrate again, as in other, previously recorded instances,[7] the importance of conformational factors for the position of the *cis-trans* equilibrium in substituted hydrindan-1-ones.

A polycyclic compound fairly analogous to the C/D *cis* dihydro derivative VII in steric respects, namely B-norcoprostan-3α-ol-6-one (XIV), has recently been examined by Dauben *et al.*[8] in regard to its behavior on treatment with alkali at room temperature. The A/B ring system of XIV resembles the C/D system of the L-enantiomorph of VII in that in both the 5-membered ring is fused in *trans-anti-cis* fashion to another cyclohexane ring, and the terminal 6-membered ring carries an

[7] N. L. Allinger, R. B. Hermann and C. Djerassi, *J. Org. Chem.* **25**, 922 (1960); J. F. Biellmann and G. Ourisson, *Tetrahedron Letters* No. 18, 4 (1960); cf. also D. H. R. Barton and G. A. Morrison, *Progress in the Chemistry of Natural Products* Vol 19; pp. 178–182. Springer-Verlag, Vienna (1961).

equatorial substituent γ to the keto group. Under conditions similar to those used in our equilibrium experiments (methanolic KOH at room temp, 18 hr), this compound was converted to the extent of about 50%, not to the 5α-epimer, but to an 8-*iso* compound (XV) in which the configuration at C-5 was left undefined. The reasons for



XIV XV XVI (5β) XVII (5α)

this unexpected behavior are not clear, since there are more unfavorable interactions in XV than in the A/B *trans*-linked 5-epimer of XIV. At any rate, the greater stability of VII under these conditions, in spite of the presence of the axial 17a-methyl substituent, must be ascribed to the stabilizing influence of the much larger equatorial 17-side chain substituent, as compared with the equatorial 3α-hydroxyl group in XIV.

The 3,6-diketone XVI corresponding to XIV, which is comparable to the olefin V in that the carbon atom γ to the keto group in the 5-membered ring (C-3) in trigonal, is regarded as the most stable isomer,[9] although this is not exactly borne out by the preparative experiment of Dauben *et al.*,[8] who treated the A/B-*trans-isomer*, B-norcholestane-3,6-dione (XVII), with methanolic alkali at room temperature and obtained from 125 mg of XVII after chromatography only 42 mg of an oil from which pure XVI was isolated after crystallization and recrystallization in unspecified yield. However, these authors also showed that the 8-*iso*-3,6-diketone corresponding to XV is converted to the A/B *cis*-diketone XVI in 77% yield under these conditions, and thus XVI is certainly the more stable isomer in respect to the 8-*iso*-diketone. That, in contrast, the equilibrium V $\leftrightarrows$ VI is greatly in favour of the C/D-*trans* compound VI may have its cause in the greater number of unfavorable interactions in either of the two forms A and B of V, as well as in the fact that in both forms ring C is a boat, as compared with XVI, in which, as the model shows, ring A can very well exist as a slightly distorted chair, and the unfavorable interactions caused by the boat character of ring D in both the A and B forms of V are therefore lacking.

The *a priori* very remote possibility that the isomerization of V to VI may involve, in analogy to the reaction XIV $\rightarrow$ XV, a change in the B/C-ring junction, i.e., in this case epimerization of carbon atom 9, is excluded, *inter alia*, by the fact that the 19-methyl signals in the NMR spectra of Va and VIa appear at nearly the same τ values (singlets for 3 H at τ 9·13 and 9·11), slightly shifted downfield from the position (τ 9·18) this signal occupies in the spectrum of diacetyltetrahydrojervine. In contrast, the corresponding value in the spectrum of N-acetyl-11-keto-5β(?)-dihydro-9β-veratramin-3-one[10] is τ 8·45, which should be compared with τ 8·97 in

[8] W. G. Dauben, G. A. Boswell, Jr., W. Templeton and J. W. McFarland, *J. Org. Chem.* **85**, 2302 (1963).

[9] L. F. Fieser, *J. Amer. Chem. Soc.* **75**, 4386 (1953); W. G. Dauben and G. J. Fonken, *Ibid.* **78**, 4736 (1956).

[10] D. M. Bailey, D. P. G. Hamon and W. S. Johnson, *Tetrahedron Letters* No. 9, 55 (1963).

that of N-acetyl-11-keto-5α-dihydroveratramine having the normal 9α-configuration.[11]

Since tetrahydrojervine (III) is transformed to the acetolysis product Va by a reaction which does not affect the configuration at C-13, it must likewise have the 13α-configuration. It does not seem to be epimerized at this carbon atom by alkali at 22° even to the slight extent observed with the comparable C/D *cis* dihydro compound VII, as the rotation of N-acetyltetrahydrojervine showed no change whatsoever under the conditions used in our equilibration experiments on the pairs Va-VIb and VIIb-VIII, and the N-acetyl derivative is obtained in about the same high yield in its preparation from the 3,N-diacetate with hot alkali as when it is made by N-acetylation of the free base with acetic anhydride and methanol.[12] This stability cannot be used, however, as an argument, as in the case of VII, in favour of the side chain being equatorial and hence having the β-configuration, because with the side chain linked back in spirane fashion to C-17 through the ether oxygen of ring E, there exist always two unfavorable *gauche* interactions between either the side chain or the oxygen and C-13 and C-15 no matter whether the former is β- or α-oriented, and hence (considering only these interactions) there should be no difference in stability between the two epimeric spirane structures. However, the scale models also show that in the isomer in which the side chain is α and axial the 21-methyl group approaches the 15α-hydrogen almost to bonding distance, while the 17-epimeric structure, with the side chain β- and equatorial, is devoid of unfavorable steric interactions. It may therefore be concluded that in tetrahydrojervine and hence in jervine itself the side chain is β-oriented, as has been postulated on biogenetic grounds.[2,*]

EXPERIMENTAL

Equilibrium measurements. The compounds used in the mutarotation experiments (Va, VIb, VIIb and VIII) were quickly dissolved in an 1:1 mixture of methanol-tetrahydrofuran containing 2% KOH so as to make their concentrations 0·9–1·0%. (The solvent mixture had to be used on account of the low solubility of the N-acetyl derivatives in methanolic KOH.) The solutions were transferred as quickly as possible to an 1 dm polarimeter tube, whereupon the initial (2–3 min) and subsequent rotation readings were taken at suitable intervals. The temperature during all these operations was 22–23°.

It was not possible to use as the initial $[\alpha]_D$ in the calculations the $[\alpha]_D$ determined in the solvent mixture containing no alkali, since in the case of VIIb and VIII these values widely diverged from the initial value determined in the alkali-containing solutions (see data below).

Compound Va (acetolysis product, triacetate[4]) m.p. 233–234° (corr); $[\alpha]_D^{22}$ −68° (chlf); −44·7° (CH_3OH-THF); mutarotation: −44·5° (initial), −16·4° (1 h), −2·0° (2 h), +1·2° (3·5 h), +1·5° (24 h).

Compound VIb (*iso*-N-acetate), m.p. 229–231°, $[\alpha]_D^{22}$ +16·7° (chlf)[4], +14·6° (CH_3OH-THF); mutarotation: +15·1° (initial), +6·5° (1 h), +2·2° (3 h), +3·6° (6 h), +1·7° (24 h).

Compound VIIb (dihydro derivative of V, side chain β, N-acetate), m.p. 271–273°, $[\alpha]_D^{22}$ −46° (chlf), −18·3° (CH_3OH-THF); mutarotation: −29·3° (initial), −28·6° (1 h), −26·3° (3 h), −25·2° (5 h), −25·0° (7 h).

* *Addendum to proof:* J.Fajkoš, J. Joska and F. Šorm have recently shown [*Coll. Czechoslov. Chem. Comm.* **29**, 652 (1964)] that the 8α-stereoisomer XV derived from 3α-hydroxy-8α-B-norcoprostan-6-one (XIV) has likewise the 5β-configuration, and furthermore that the order of stability in the 3-hydroxy-6-keto compounds of this series is 5β,8α > 5β,8β > 5α,8β, whereas of the 3,6-diones the 5β,8β-isomer is the most stable one.

[11] Our own measurement, 60 Mc, in deuterochloroform.

[12] B. M. Iselin and O. Wintersteiner, *J. Amer. Chem. Soc.* **76**, 5616 (1954).

When the corresponding triacetate (VIIa), m.p. 241–243°, $[\alpha]_D^{23}$ −39° (chlf),[4] −15·4° (CH_3OH-THF) was similarly treated, $[\alpha]_D$ fell from the initial value −20·3° to −29·2° at 3 hr, and then rose to −22·2° at 6 hr, where it remained constant (22 h). The initial fall must in part represent the saponification of the 2 acetoxy groups; $[\alpha]_D$ at equilibrium when corrected for the loss of the 2 acetyl groups is −26·1°, somewhat higher than the equilibrium value for VIIb.

Compound VIII (dihydro derivative of VIa, side chain β, triacetate), m.p. 227–229°, $[\alpha]_D^{20}$ −18·5° (chlf),[4] −6·8° (CH_3OH-THF); mutarotation: +9·1° (initial), +11·3° (1 h), +2·3° (2 h), −2·4° (3 h), −10·7° (7 h), −22·4° (23 h), −22·6° (29 h); calc. as N-acetate, −26·3°.

Compound IXa (dihydro derivative of VIa, side chain α, triacetate), amorphous $[\alpha]_D^{23}$ −18·7° (chlf), −21·6° (CH_3OH-THF); mutarotation: −20·7° (initial), −15·8° (1 h), −14·9° (2 h), −15·2° (18 h). Clearly the change in the first hour represents the O-deacetylation, and the N-acetyl derivative IXb thus formed (m.p. 237–240°, $[\alpha]_D^{23}$ −15·7° (chlf)) is not further changed by alkali.

Calculation. Since the reactions Va → VIb and VIII → VIIb entail a change in mol wt corresponding to the loss of 2 acetyl groups, the rotation values entering the calculations had to be expressed as molecular rotations $[M]_D$. Furthermore, as mentioned in Footnote 6, the calculation of the equilibrium position involves the assumption that the molecular rotation change accompanying the O-deacetylation is negligible in comparison with the mutarotation change. This is nearly true for Δ[M] VIIa → VIIb (= 0) and Δ[M] IXa → IXb (= ±12°) when based on $[\alpha]_D$s measured in chloroform solution, but for the olefin VI the difference $\Delta[M]_D$ VIa → VIb (in chloroform) is −65° and hence not negligible. Moreover, Δ[M] VIIa → VIIb when measured in the alkali-containing solvent mixture is −27°, and Δ[M] IXa → IXb in the same medium +31°. However, as the examples below show, when corrections of this order of magnitude are applied to the starting rotations of the triacetates, the calculated percentages of the two compounds present in the equilibrium mixture change by only a few percent, and while this produces considerable differences in the *cis/trans* ratios, it does not impair the conclusion that in the equilibrium of the olefin pair V-VI the *trans*-isomer VI greatly preponderates, while the equilibrium between the saturated compounds VII and VIII overwhelmingly favours the *cis* isomer VII.

The percentage composition of the equilibrium mixture was calculated by using the formula $x = 100\,([M]_E - [M]_2)/([M]_1 - [M]_2)$, in which $[M]_E$ is the molecular rotation at equilibrium, $[M]_1$ that of the starting compound, $[M]_2$ that of the compound formed, and x the percentage of the starting compound remaining at equilibrium.

Example

Equilibrium Va ⇄ VIb, with Va as the starting product: $[M]_E = +1{\cdot}6° \times 5{\cdot}56 = 8{\cdot}9°$; $[M]_1 = 44{\cdot}7° \times 5{\cdot}56 = -248°$; $[M]_2 = +14{\cdot}6 \times 4{\cdot}72 = +68{\cdot}9°$; x = 19; 100 − x = 81; K *trans/cis* = 4·27. The calculation for the experiment in which VIb was used as the starting product would give practically the same value, since the values for $[\alpha]_E$ are very small and practically identical in both experiments, and hence the difference between the two $[M]_E$ values is only about 1°. If in the above computation $[M]_1$ is corrected for an assumed Δ[M] = +65° for the O-deacetylation of V, then x becomes 15·7, and K *trans/cis* 5·36.

Equilibrium VIIb ⇄ VIII, starting with VIII: x = 6·7; 100 − x = 93·3; K *cis/trans* = 14; starting with VIIb: x = 10·8; 100 − x = 89·2; K *cis/trans* = 8·26; if $[M]_1$ in the former computation is corrected for an assumed Δ[M] = +31° for the O-deacetylation, then x = 9·2, 100 − x = 90·8, K *cis/trans* = 9·9.

N-*Acetyl derivative* IXb *from triacetate* IXa (13β, side chain α). The amorphous triacetate IXb used as the starting product was obtained by chromatography of the crude hydrogenation product of the olefin VIa.[4] It had $[\alpha]_D^{21}$ −18·7° (*c*, 0·98 in chlf); lit.[4] −14°. (Found: C, 71·55; H, 9·36. Calc. for $C_{33}H_{51}O_6N$ (557·7): C, 71·06; H, 9·22%).

A solution of this product (43 mg) in 5% methanolic KOH (8 ml) was allowed to stand overnight, and then after dilution with water extracted with chloroform. The washed (dil. HCl, H_2O) and dried extract was brought to dryness, and the residue was recrystallized twice from ethyl acetate (29 mg, m.p. 240–243° (corr); $[\alpha]_D^{23}$ −15·7° (*c*, 1·119 in chlf)). (Found: C, 73·27; H, 10·07. Calc. for $C_{29}H_{47}O_4N$ (473·7): C, 73·53; H, 10·00%).

Acetylation of this N-acetyl derivative in pyridine and acetic anhydride at room temp overnight yielded the amorphous triacetate IXa exhibiting the same rotation (−18·1° in chlf) and IR spectrum as the starting product.