ous solution with chloroform led to the isolation of VI. Formation of VI from VII most probably occurs via a Hofmann-type elimination.

These data conclusively demonstrate the existence of two discrete carbonium ion intermediates under conditions of the elimination reaction and provide strong evidence for their intervention under the solvolysis conditions in the sequence I → II → III. The difference between these two intermediates must lie in their different internuclear distances and in the orientation of the C_{19}-methano bridge[13].

Zusammenfassung. Die Existenz von zwei verschiedenen isomeren Homoallylkationen in der Umlagerung von Steroid-Δ^5-19-Methansulfonsäure-Estern zu 5β,19-cyclo-6-hydroxylierten Steroiden und deren Umlagerung zu $\Delta^5(^{10})$-B-homo-7-hydroxylierten Steroiden wurde bewiesen, und eine neue Art der Homoallylumlagerung eines $\Delta^5(^{10})$-B-homo-7-hydroxylierten Steroids zum 5β,6β-Methano-9-en und zum 5β,6β-Methano-10β-ol wurde beobachtet.

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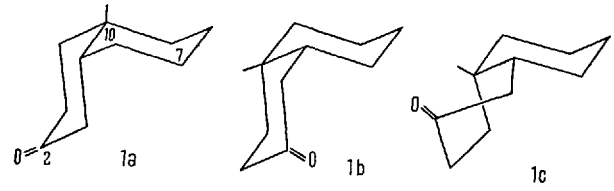
Conformational Studies of *cis*-10-Methyl-2-decalones

In the past eight years, the conformation equilibrium of *cis*-10-methyl-2-decalone (1) has been evaluated by conformational concepts[1] and by ORD measurements[2]. On the basis of the conformational postulates it was suggested that such a ketone would assume the *non-steroidal* conformation 1b, but subsequently the *steroidal* conformation 1a was indicated on the basis of ORD studies. Recently, this problem was reinvestigated[3] and ORD and temperature dependent circular dichroism measurements were performed on *cis*-7,7,10-trimethyl-2-decalone and on *cis*-7α-isopropyl-10β-methyl-2-decalone. These studies led the investigators to the conclusion that in these substituted *cis*-10-methyl-2-decalones the *non-steroidal* all-chair conformation 1b probably played an unimportant role in the conformational equilibrium and a twist conformation (for example 1c) was favored. It was also suggested that the only other and rather remote possibility was that the 'non-steroid' conformer 1b was indeed predominant and the Cotton curve was controlled by a smaller amount of a conformer with an extremely powerful amplitude. This possibility has now been evaluated and, indeed, shown to be correct.



In conformations 1a, 1b, and 1c, the relative position of the C-10 methyl group with respect to the carbonyl group is different and the position of the methyl group should be indicated by its chemical shift in its NMR-spectrum. For example, in the steroids it has been found that when the C-19 methyl group is axial to the ring (in a chair conformation) having a carbonyl group at C-3 (i.e. A/B-*trans*-3-keto-steroid) its resonance band is shifted downfield by 0.22 ppm as compared to the chemical shift of the C-19 methyl group in the parent hydrocarbon[4-6]. When the C-19 methyl group is equatorial to the ring (in a chair conformation) the downfield shift is only 0.11 ppm. On the other hand, in a *twist* conformation the C-19 methyl group is diamagnetically shielded by the C-3 carbonyl group and its resonance band is approximately at the same position as in the parent hydrocarbon[6].

In order to employ this method of analysis in the *cis*-10-methyl-2-decalone series, it was first necessary to see if these simple models of steroids followed the downfield paramagnetic shift. The data obtained are summarized in the Table.

Chemical shifts of C_{10}-methyl protons[a]

Compound	τ (ppm)	Δ ppm (one-ane)	Compound	τ (ppm)	Δ ppm (one-ane)
A/B-*trans*			A/B-*cis*		
Cholestane	9.23		Coprostane	9.08	
3-keto	9.01	−0.22	3-keto	8.97	−0.11
10-Methyl-decalin	9.17		10-Methyl-decalin	9.05	
2-keto	8.97	−0.20	2-keto	8.83	−0.22
4-keto	8.93	−0.24	4-keto	8.83	−0.22
			2-keto-7,7-dimethyl	8.76	−0.29
			7α-Isopropyl-10β-methyl-decalin	9.05	
			2-keto	8.78	−0.27

[a] The spectra were obtained with carbon tetrachloride solutions and calibrated with tetramethylsilane as an internal standard.

[1] W. KLYNE, Exper. *12*, 119 (1956).
[2] C. DJERASSI and D. MARSHALL, J. Am. chem. Soc. *80*, 3986 (1958).
[3] C. DJERASSI, J. BURAKEVICH, J. W. CHAMBERLIN, D. ELAD, T. TODA, and G. STORK, J. Am. chem. Soc. *86*, 465 (1964).
[4] R. F. ZÜRCHER, Helv. chim. Acta *44*, 1380 (1961).
[5] E. R. MALINOSKI, M. S. MANHAS, G. H. MÜLLER, and A. K. BOSE, Tetrahedron Letters *1963*, 1161.
[6] M. GORODETSKY and Y. MAZUR, Tetrahedron Letters *1964*, 227.

In the *trans*-10-methyldecalin series, compounds which possess a chair-chair conformation, the axial methyl group is shifted downfield by 0.22 ppm when the carbonyl group is placed in the 2-position. This value is in good agreement with the value found in the steroid series and this result indicates that the steroid chemical shift data are applicable to the 10-methyl-decalin series. We have now also shown that the ORD curves for *cis*- and *trans*-10-methyl-2-decalones obtained in carbon tetrachloride solution were not significantly different from those found in methanol and dioxane solution.

In the *cis*-10-methyldecalin series, it was found (see Table) that introduction of a carbonyl group at the C-2 position shifted the C-10 methyl resonance downfield by 0.22–0.29 ppm. These values are to be compared with values of 0.11 ppm found in the coprostane series for A/B-*cis* compounds possessing the two chair conformations arranged in the steroidal form 1a. The decalin values found indicate that the spatial arrangement between the carbonyl and C-10 methyl group in the *cis*-10-methyl-2-decalones is similar to that found in the *non-steroidal* conformation 1b where the C-10 methyl group is axial to the ring holding the carbonyl group. Such a spatial arrangement has been assigned earlier on the basis of conformational analysis[1]. If the *twist* conformation 1c favored by ORD studies were the sole or major conformation, the angular methyl group would be diamagnetically shielded by the carbonyl group and would have its resonance band at about the same position as in the parent hydrocarbon[6].

It previously had been demonstrated by low temperature circular dichroism technique[3] that with the *cis*-7,7-dimethyl- and *cis*-7α-isopropyl-10-methyl-2-decalones one is dealing with a mixture of conformers. That a similar situation also exists for the parent *cis*-10-methyl-2-decalone has now been demonstrated by a study of the change of its NMR-spectrum with temperature. It was found that at – 20° to – 30° there was a band broadening and at – 65° to – 70° there was an increase in the fine structure of the spectrum.

Thus, the room temperature NMR-spectrum of the *cis*-10-methyl-2-decalones indicate that the *non-steroidal* conformation 1b is a major contributor to the conformational equilibrium. *The sign of the Cotton curve must be controlled by a conformer present in minor amounts and which has a large rotational value*[7]. Indeed, the twist conformation 1c could be such a minor contributor since it has been shown that such a conformation has a much higher Cotton effect magnitude than the standard chair form of cyclohexanones[8].

In the Table are also listed the chemical shifts of the related *cis*- and *trans*-10-methyl-4-decalones. Here again the chemical shifts of the two isomeric ketones relative to their parent hydrocarbons are about the same. As in the 2-decalone cases, it would appear that in the *cis* isomer the *non-steroidal* conformation predominates.

In all of the NMR-studies, however, it is realized that such a spectral investigation does not permit an unequivocal analysis of the conformations present. The temperature dependence of the CD studies does show that the change in free energy with temperature is greater for the lesser conformation (or conformations) which controls the sign of the ORD or CD curve. The entropy of the minor conformation (or conformations) must be larger than that of the major conformation and such a relationship would be expected between a twist and a chair conformation[9,10].

Zusammenfassung. Im Kernresonanzspektrum einiger substituierter *cis*-2-Decalone wurden die chemischen Verschiebungen angulärer Methylgruppen untersucht. Dabei wurde festgestellt, dass die Verbindungen vorwiegend in der nicht-steroidalen Sessel-Sessel-Konformation vorliegen. Das Vorzeichen der ORD Cotton-Kurven dieser Ketone muss durch das untergeordnete Vorhandensein einer Konformation sehr starker Amplitude, wie z. B. der Twist-Form, bedingt sein.

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[7] This alternative was in fact considered in the early study (ref. [3], footnote 16) as a possible but less likely explanation for the observed ORD and CD data.

[8] C. DJERASSI and W. KLYNE, Proc. nat. Acad. Sci., US *48*, 1093 (1962).

[9] We wish to thank Prof. F. R. JENSEN and Mrs. BARBARA BECK for the low temperature study and Mr. J. KARLINER for the preparation of 7-isopropyl-10β-methyldecalin. This work was supported in part by Grants A-709 and GM-06840 from the National Institutes of Health of the US Public Health Service.

[10] Added in proof: Since this paper was submitted, ELLIOTT, ROBINSON, and RIDELL[11], using the NMR-method, have arrived at similar conclusions.

[11] D. R. ELLIOTT, M. J. T. ROBINSON, and F. G. RIDELL, Tetrahedron Letters *1965*, 1693.

Alkaloid Studies LV[1]. 19-Dehydroyohimbine, a Novel Alkaloid from *Aspidosperma pyricollum*

The recent encounter[2] in various *Aspidosperma* species of congeners of the biogenetically intriguing alkaloid uleine (I)[3] prompted a reinvestigation – using more refined separation techniques coupled with mass spectrometry[4] – of the bark of *Aspidosperma pyricollum* Muell.-Arg. from which only uleine (I) had been isolated previously[5]. In the present study, aside from uleine (I), there was encountered (–)-apparicine (II)[6], a trace of demethyl-aspidospermine (III)[7], yohimbine (IV), β-yohimbine (V), and a novel alkaloid, which in the sequel will be shown to possess the structure of 19-dehydroyohimbine (VI). The latter three substances occurred only in the strongly basic alkaloid fraction and represent the three principal alkaloids of this plant.

The new alkaloid, m.p. 245° (dec.), $[\alpha]_D^{27}$ + 106° (c, 0.53 in pyridine), exhibited an UV-absorption spectrum (λ_{max}^{EtOH} 226, 283, 293 mμ, log ε 4.48, 3.85, 3.77) very similar to that of yohimbine (IV) as well as IR-bands at 2.90 μ (NH) and 5.80 μ. The empirical formula $C_{21}H_{24}N_2O_3$ (Found: C 71.00, H 6.90, N 7.74, mol. weight 352 (mass spec.); calcd. C 71.57, H 6.86, N 7.95, mol. weight 352)