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EQUILIBRIUM COMPOSITION AND PROPERTIES OF CEDRANE EPIMERS*

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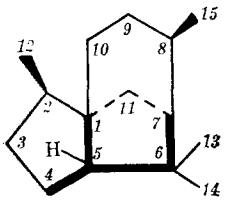
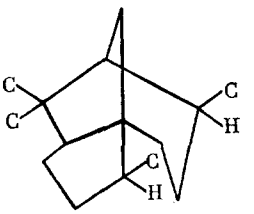
CEDRANE, or 2,6,6,8-tetramethyltricyclo[5.3.1.$0^{1,5}$]undecane, is a well-known tricyclic sesquiterpene hydrocarbon. The presence of hydrocarbons of this structure in various caustobioliths is confirmed [1], and a precursor of this homologous series—tricyclo[5.3.1.$0^{1,5}$]undecane is known in petroleum [2].

Alkyl-substituted cyclanes usually occur as thermodynamically stable epimers, accordingly information concerning their relative thermodynamic stability is required in relation to their occurrence in crude oil. This paper is devoted to this problem and to catalytic synthesis of the various cedrane epimers:

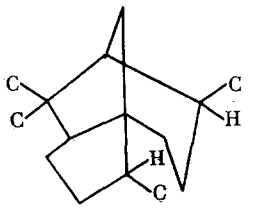
Structural formulae of three-dimensional cedrane epimers are as follows:



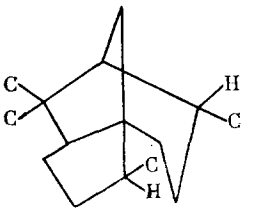
1*S*, 2*R*, 5*S*, 7*R*, 8*R*
(*exo*, *endo*)



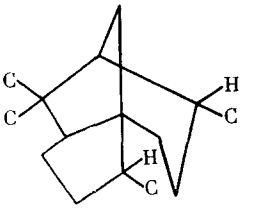
(*endo*, *exo*)



(*exo*, *exo*)



(*endo*, *endo*)



(*exo*, *endo*)

The expected number of diastereomers (epimers) in the equilibrium mixture is four, since the hydrocarbon has two chiral centres ($C_{(2)}$ and $C_{(8)}$) that are subject to epimerization. Epimerization of $C_{(1)}$, $C_{(5)}$ and $C_{(7)}$ is thermodynamically unlikely and accordingly has not been examined by the authors.

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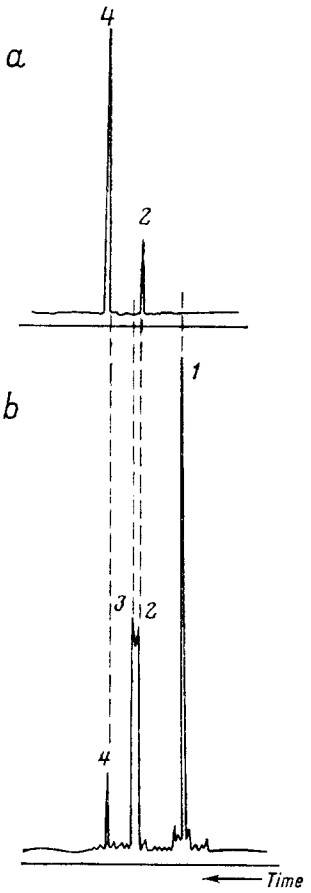
It is known that natural (+) cedrol (8-hydroxycedrane) has 1*S*, 2*R*, 5*S*, 7*R* and 8*R* configuration. However, the conventional stereochemical nomenclature of bi- and tricyclic hydrocarbons extensively used in previous studies [3] is more convenient. Epimers of varying configuration of $C_{(8)}$ are designated *endo*- and *exo*-diastereomers of the corresponding 2-methylbicyclo[3.2.1]octanes, while epimers with varying configuration of $C_{(2)}$ relate to the *endo*- and *exo*-2-methylbicyclo[3.3.0]octanes.

EXPERIMENTAL

Cedrol acetate (+) was conveniently transformed at 400°C into cedrane (mixture of two positional isomers). Cedrane was obtained by hydrogenation of cedrane in the presence of Raney nickel (150°C, 10 MPa) and a chromatogram of this material(*a*) is shown in the Figure. (Analysis: capillary column, 80 m, Apiezone L at 175°C.)



Chromatogram of initial (*a*) and equilibrium (*b*) mixtures of cedrane epimers. See text for interpretation of peaks.

TABLE 1. CHEMICAL SHIFTS FOR C^{13} NUCLEI OF CEDRANE EPIMERS

Peak No. in Figure	Configuration	Method	Carbon atoms														
			$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	C_{7}	$C_{(8)}$	$C_{(9)}$	$C_{(10)}$	$C_{11)}$	$C_{(12)}$	$C_{(13)}$	$C_{(14)}$	$C_{(15)}$
1	*eneo, exo* (2*S*, 8*S*)	Experiment	56·9	43·0	34·7	24·4	54·7	43·6	54·2	29·3	27·9	37·9	31·3	14·1	26·9	25·1	20·7
2	*exo, exo,* (2*R*, 8*S*)	,,	55·2	42·7	37·3	25·9	57·0	42·4	55·8	29·4	27·1	30·5	38·9	15·5	27·8	25·0	20·6
		Calculation	55·0	42·6	37·4	25·9	58·1	42·0	55·0	30·0	26·8	32·0	40·0	15·0	27·0	25·0	20·0
4	*exo, endo* (2*R*, 8*S*)	Experiment	54·6	42·6	37·4	25·9	58·1	44·2	56·0	38·9	29·8	34·1	48·0	15·6	27·4	29·2	22·0
		Calculation	56·0	41·0	36·0	28·0	59·0	42·0	54·0	39·0	30·0	34·3	48·0	15·0	27·0	29·0	23·0

TABLE 2. MASS-SPECTRA OF CEDRANE EPIMERS

Peak No. in Figure	Configuration	Main fragment ions and their relative intensity, %
1	*endo, exo* (2*S*, 8*S*)	206(30), 191(13), 163(80), 150(17), 135(25), 122(28), 121(46), 108(100), 107(39), 93(64), 82(68), 81(49), 95(61).
2	*exo, exo* (2*R*, 8*S*)	206(29), 191(14), 163(72), 150(17), 135(39), 122(51), 121(60), 108(81) 107(43), 95(75), 93(60), 82(100) 81(60).
4	*exo, endo* (2*R*, 8*S*)	206(20), 191(13), 163(34), 150(18), 135(21), 122(35), 121(42) 108(15), 107(25) 95(48), 93(35), 82(100), 81(40).

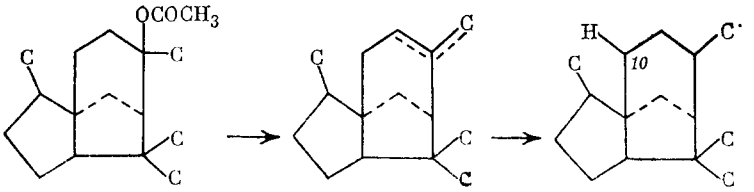
Note. Maximum ion intensity for epimers *1*, *2*, *4* is 8·1; 7·3; 11·5%, respectively of the total gas current.

TABLE 3. EQUILIBRIUM CONCENTRATIONS AT 563°K AND RETENTION INDICES OF CEDRANE EPIMERS

Peak No. in Figure	Epimer	Retention index (Apiezone, 175°C)	Equilibrium concentration, %
1	*endo*-2-Methyl, *exo*-8-methyl (2*S*, 8*S*)	1514	56·0
2	*exo*-2-Methyl, *exo*-8-methyl (2*R*, 8*S*)	1532	19·0
3	*endo*-2-Methyl, *endo*-8-methyl (2*S*, 8*R*)	1536	17·0
4	*exo*-2-Methyl, *endo*-8-methyl (2*R*, 8*R*)	1545	9·0

These reactions do not affect the configuration of the chiral centre at $C_{(2)}$, which determines in the initial acetate the *exo*-orientation of the methyl substituent in the bicyclo[3.3.0]octane system.

The chromatogram (Fig. *a*), shows that the cedrane obtained consisted of two epimers (peaks *2* and *4*) with a 1 : 4 ratio. As expected, these hydrocarbons are characterized by the configuration of the chiral centre $C_{(8)}$, i.e. are *exo*-(*a*) and *endo*-(*e*) 8-methylepimers and correspond to *exo*-2-methyl- and *endo*-2-methylbicyclo [3.2.1]octanes. C^{13} NMR spectra (Table 1) confirmed this and enabled the *endo*-configuration of the methyl substituent at $C_{(8)}$ to be assigned mainly to an epimer of higher boiling point (peak *4*) and the *exo*-configuration—to an epimer of lower boiling point (peak *2*). [These C^{13} NMR spectra came from a Brooker SKhR-200 pulse spectrometer at 50·31 MHz using TMS as internal standard]. The equatorial orientation of the methyl at $C_{(8)}$ in cedrane [from the reduction of cedrane (Ni-Re, 100°C, 10 MPa] has been described previously [4]. The *exo*-2-methyl-*endo*-8-methyl and *exo*-2-methyl-*exo*-8-methylepimer mixture of cedrane obtained was subjected to equilibrium configuration isomerization. [Liquid phase at 563°K for 4 hr in a steel autoclave under hydrogen 5 MPa, catalyst platinum on charcoal]. The other two epimers were obtained and the chromatogram of the equilibrium mixture (*b*) is shown in the Figure.



Details of the C^{13} NMR spectra, are shown in Table 1 and mass spectra of three epimer cedranes, in Table 2. [Mass spectra, from an LKB-2091 chromatomass-spectrometer and computer system (LKB-2130), with a 60 m glass capillary column and SP-2100 as fixed phase].

Examination of the stereochemical features and the thermodynamic stability of individual epimers shows that the newly formed epimers 1 and 3 have *endo*-orientation of the methyl substituent at $C_{(2)}$. Among epimer pairs with different con-

figuration at the chiral centre ($C_{(8)}$ a much higher hydrocarbon stability with *exo*-(*a*) orientation of methyl, could be assumed since the *endo*-(*e*) isomer shows strong interaction between two methyl groups (pentane interaction), similar to *endo*, *endo*-2,7-dimethylbicyclo[3.2.1] octane [3], as confirmed by C^{13} NMR for diastereoisomers 2 and 4 (Table 3).

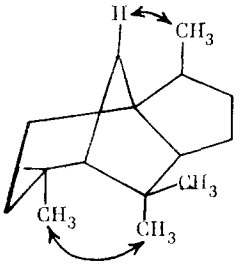


Table 3 shows retention indices and equilibrium concentrations of cedrane epimers.

Whilst the relative thermodynamic stability of epimers with varying configuration of $C_{(8)}$ was generally close to the value expected on the basis of conformation analysis (in *endo*-epimer pentane interaction is 15 kJ/mole, in the *exo*-epimer two tapered butane interactions are 7·5 kJ/mole), a much higher stability of *endo*-2-methylepimers was somewhat unexpected, especially as in corresponding 1,2-dimethylbicyclo[3.3.0]octanes the stability of epimers is quite similar [3]. But, due to distortions of dihedral angles these relationships could hardly be transferred from bicyclic to tricyclic systems. Molecular models indicate that in cedrane, the *exo*-2-methylepimers (natural configuration), show interaction between the methyl radical and the hydrogen atom at $C_{(10)}$, while in the *endo*-2-methylepimers interaction between the methyl radical and hydrogen atoms at $C_{(11)}$ is less marked.

SUMMARY

1. Equilibrium configuration isomerization of cedrane was carried out at 563°K giving a mixture of four diastereomers of different steric configuration of methyl substituents, at $C_{(2)}$ and $C_{(8)}$.

2. The composition of the equilibrium mixture was determined ^{13}C NMR and mass-spectral data are given for the cedrane epimers. It established relative thermodynamic stability decreasing in the order of epimers: *endo*, *exo*>*exo*, *exo*>*endo*, *endo*>*exo*, *endo*.

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