EQUILIBRIUM TRANSFORMATIONS OF p-MENTHENES

Z. A. Filippenko, G. N. Roganov, and V. V. Bazyl'chik

UDC 547.596.7+541.62

The equilibrium isomerization of p-menth-1-ene (M-1), p-menth-3-ene (M-3), and p-menth-4(8)-ene [M-4(8)] in the temperature interval from 250 to 350°C has been studied by the pulsed method in a microreactor in the line of a gas chromatograph (with argon as the carrier gas). We have described the experimental procedure previously [1]. As the initial materials we used concentrations of M-1 (44%), M-3 (76%), and M-4(8) (44%), and also of cis-p-menth-8-ene (31%) obtained by the hydrogenation of the corresponding aromatic hydrocarbons and containing, in addition to the main substance in each case, impurities of isomeric nature and also, for M-1 and M-4(8), p-cymene. The catalyst used was alumina with 5 wt. % of cobalt. The time of contact of the substances with the catalyst was varied by a factor of 1.5-2. The amount of byproducts formed as a function of the temperature and residence time of the initial substances in the reaction zone ranged between 15 and 40%. The formation of cymene did not exceed 25% even at 350°C.

A materials balance of the experiments was drawn up with an accuracy of ±5% molar. The results of each equilibrium isomerization are given in Table 1. From these results for the transformations M-1 $\rightleftarrows$ M-3 and M-1 $\rightleftarrows$ M-4(8) by the method of least squares were found the values of the enthalpy (-9.2 ± 0.9 and 10.0 ± 1.0 kJ·mol^{-1}, respectively) and the entropy (-13.1 ± 1.7 and 9.7 ± 1.7 J·mole^{-1}·K^{-1}) of the reactions and estimated the errors in these values.

The relative characteristics of the dynamic stabilities of the p-menthenes obtained can be explained from the aspects of conformational analysis. Thus, in M-1 and M-3 the substituents at the double bond lie in its plane and have only a slight influence on the energy stability of the compound [2], while the increase in the size of the alkyl group in position 4 of the half-chair conformatin [3] on passing from M-3 to M-1 leads to destabilization. In any case, the replacement of a methyl group by an isopropyl group in the cyclohexane ring lowers the relative stability of the compound by 4-5 kJ·mole^{-1} [4]. A calculation of the strain energies of hydrocarbons similar in structure to M-4(8) and M-1 with the aid of the method of group contributions shows that the strain energy of the M-4(8) ring is approximately 9 kJ·mole^{-1} greater than that of M-1. This agrees with the results that we have obtained.

The difference in the entropies of the isomers is due mainly to the difference in the entropies of mixing of the conformers and the parameters of internal rotation of the alkyl groups.

TABLE 1. Equilibrium Compositions of Isomeric Mixtures of p-Methenes

T, °C	Volume of the layer of catalyst, mm^3	Number of expts.	Composition of the equilibrium mixture, %-molar		
			menth-3-ene	menth-4(8)-ene	menth-1-ene
250	502—754	13	56,3±0,3	10,8±0,2	33,0±0,2
275	502	6	54,8±0,4	11,9±0,2	33,3±0,3
300	502—754	5	50,8±0,3	14,1±0,2	35,1±0,3
325	502—754	14	48,0±0,3	15,8±0,2	36,2±0,3
350	502—754	10	44,2±1,0	17,6±0,4	38,3±0,7

Mogilev Technological Institute. I. N. Ul'yanov Chuvash State University, Cheboksary. Translated from Khimiya Prirodynkh Soedinenii, No. 6, pp. 878-879, November-December, 1988. Original article submitted April 15, 1988.

LITERATURE CITED

1. Z. A. Filippenko, O. M. Baranov, G. N. Roganov, and G. Ya. Kabo, Khim. Prir. Soedin., 51 (1985).
2. U. Burkert and N. L. Allinger, Molecular Mechanisms, ACS Monograph 177 (1982) [Russian translation: Mir, Moscow (1986), p. 364].
3. A. N. Vereshchagin, Usp. Khim., 52, No. 11, 1879 (1983).
4. E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, Conformational Analysis, Interscience, New York (1965) [Russian translation: Mir, Moscow (1969), p. 592].

PULCHELLIN C FROM *Inula britannica*

S. V. Serkerov and N. F. Mir-Babaev

UDC 547.992:547.37

The sequiterpene lactone britanin has been isolated previously [1] from *Inula britannica* L., and from the variety *chinensis* of the species the sesquiterpene lactones tomentosin, ivalin, 4-epi-isoinuviscolide, gaillardin, and inuchinenolides A, B, and C [2].

We have investigated the sesquiterpene lactones of the epigeal part of this plant collected in June, 1984, close to the village of Astrakhanovka, Shemakhinskii raion. The air-dry epigeal part (700 g) of *Inula britannica* was extracted with acetone three times. The total extractive substances obtained (5 g) were dissolved in 15 ml of chloroform and chromatographed on a column (3 × 130 cm) of alumina. The column was eluted with hexane, hexane–chloroform, chloroform, chloroform–ethyl acetate, and ethyl acetate. The volume of each fraction was 200 ml. Fraction 35, eluted by ethyl acetate, was rechromatographed on a column (0.8 × 20 cm) of silica gel (L 40/100 μm, Chemapol) with chloroform. On standing, the chloroform eluates deposited crystals which were recrystallized from aqueous ethanol. This gave 15 mg of a white crystalline substance with the composition $C_{15}H_{20}O_4$ (M^+ 264), mp 200-201°C.

The IR spectrum of the substance had absorption bands of OH groups (3600, 3490 cm^{-1}), of the CO group of an α-methylene-γ-lactone ring (1760, 1670 cm^{-1}) and of a double bond (1660 cm^{-1}). The presence in the mass spectrum of the peaks of the ions M^+, 246 ($M - H_2O$) 231 ($M - H_2O - CH_3$), and 228 ($M - H_2O - H_2O$) permitted the assumption that this substance was a diol.

According to NMR spectra (δ scale) 0 – TMS, Bruker WH-250), both hydroxy groups were of secondary nature (d, 3.85 ppm, J = 10 Hz; sx, 3.55 ppm, $J_1 = J_2 = 10$ Hz, $J_3 = 5$ Hz). One-proton signals at 4.75, 5.26 and 5.64, and 6.18 ppm showed the presence in the molecule of

TABLE 1. Chemical Shifts of the Protons of the Compounds under Investigation and of Pulchellin C

Protons	Compounds under investigation		Pulchellin C in $CDCl_3$
	in DMSO-d_6	in $CDCl_3$	
H-2	—	sx, 3,55, $J_1=J_2=10$ Hz $J=5$ Hz	m, 3,5
H-3	—	d 3,85, $J=10$ Hz	d, 3,78, $J=9$Hz
H-7	m, 3,08	m, 3,00	m, 3,00
H-8	sx, 4,52, $J=5$, $J_2=5$ $J_3=2$ Hz	sx, 4,52, $J_1=J_2=5$ Hz $J_3=2$ Hz	br.t, 4,52, $J=5$ Hz
H-13a	s, 5,75	s 5,64	d, 5,60, $J=1$ Hz
H-13b	s 5,96	s, 6,18	d, 6,18, $J=1$ Hz
H-14a	d, 5,16, $J=2$ Hz	s, 5,26	s, 5,26
H-14b	d, 4,70, $J=2$ Hz	s, 4,75	s, 4,71
CH_3-15	c, 0,68	s, 0,87	s, 0,82
—OH	d, 4,75, $J=5$ Hz		
—OH	d, 4,90, $J=5$ Hz		

A. I. Karaev Institute of Physiology, Academy of Sciences of the Azerbaidzhan SSR, Baku.
Translated from Khimiya Prirodynkh Soedinenii, No. 6, pp. 879-880, November-December, 1988. Original article submitted March 4, 1988.

0009-3130/88/2406-0752$12.50