LITERATURE CITED

1. L. P. Kuptsova and A. I. Ban'kovskii, Khim. Prir. Soedin., 128 (1970).
2. L. P. Smirnova, G. G. Zapesochnaya, V. I. Sheichenko, and A. I. Ban'kovskii, Khim. Prir. Soedin., 313 (1974).
3. R. Hegnauer, Chemotaxonomie der Pflanzen, Birkhäuser Verlag, Basel and Stuttgart, Vol. 6 (1973), p. 361.
4. J. B. Harborne, T. J. Mabry, and H. Mabry, The Flavonoids, Chapman and Hall, London (1975), p. 272.

TRANSFORMATIONS OF p-MENTHADIENES UNDER THE ACTION OF POTASSIUM tert-BUTANOLATE IN DIMETHYL SULFOXIDE

É. F. Buinova, T. R. Urbanovich,
B. G. Udarov, and L. V. Izotova

UDC 547.596.7

The products of the transformation of α- and γ-terpinenes, terpinolene, (+)-trans-isolimonene, and (+)-limonene under the action of potassium tert-butanolate in dimethyl sulfoxide contained — in addition to the α- and γ-terpinenes, isoterpinolene, p-mentha-3,8-diene and p-cymene found previously — terpinolene, α- and β-phellandrenes, p-mentha-2,4-diene (in a total amount of 1-3%), and polymers. Under these conditions, limonene is racemized. The primary products of the isomerization reaction have been identified. A supplementary scheme for the isomerization transformations of p-menthadienes is presented.

The literature contains varying opinions concerning the composition of the products of the transformation of the p-menthadienes under the action of potassium tert-butanolate in dimethyl sulfoxide. According to Ferro and Naves [1], at 100°C α-, and γ-terpinenes, terpinolenes, (−)-isolimonene, (+)-limonene, p-mentha-2,4-diene, isoterpinolene, and p-mentha-3,8-diene form p-cymene and an equilibrium mixture of four p-menthadienes: 33% of isoterpinolene, 3% of p-mentha-3,8-diene, and 50% of α- and 14% of γ-terpinenes [1]. According to other results, at 55°C, dipentene is converted into p-cymene, p-menthenes, and an equilibrium mixture of three isomers: isoterpinolene and α- and γ-terpinenes in a ratio of 3:5:1 [2]; while at 34°C (+)-isolimonene forms mainly isoterpinolene [3]. It has been reported that the amount of p-cymene [1, 2] and of p-menthenes [2] increases in the course of time and with a rise in the temperature of the reaction. A mechanism of the racemization, isomerization, and dehydration of limonene has been proposed [1].

In the present paper we give the results of a study of the composition of the products of the transformation of α-terpinene (I); γ-terpinene (II), terpinolene (III), (+)-trans-isolimonene (IV), and (+)-limonene under the action of potassium tert-butanolate in dimethyl sulfoxide as a function of the reaction time. It has been shown that this process forms p-cymene (VI), polymers, and an equilibrium mixture of eight p-menthadienes containing 47% of the terpinene (I), 16% of the terpinene (II), 32% of isoterpinolene (VII), 3.5% of p-mentha-3,8-diene (VIII), 0.4% of terpinolene, 0.4% of α-phellandrene (IX), 0.2% of β-phellandrene (X), and 0.5% of p-mentha-2,4-diene (XI).

As can be seen from Table 1, α-terpinene first forms γ-terpinene. In the course of time, its amount rises and it reaches a maximum of 23% after 10 min. Appreciable amounts of the menthanes (VII) and (X) are formed after 5 min and of the menthadienes (IX) and (XI) after 10 min. The menthadienes (III) and (VIII) are formed only after 5 h. Cymene and polymers are formed as early as the first few minutes of the reaction; their amount rises reaching 2% and 22%, respectively, after 20 h. After 30 h from the beginning of the reaction, a mixture of the above-mentioned products is formed which does not change with a further increase in the reaction time.

Institute of Physical Organic Chemistry, Academy of Sciences of the Byelorussian SSR, Minsk. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 587-591, September-October, 1982. Original article submitted November 11, 1981.

0009-3130/82/1805-0555$07.50

TABLE 1. Change in the Composition of the Transformation Products of p-Menthadienes (0.90 M solution) under the Action of Potassium tert-Butanolate (0.25 M solution) in Dimethyl Sulfoxide at 50°C as a Function of the Reaction Time

Menthadiene	Time, h	Composition of the transformation products, %									
		p-mentha-2,4-diene	α-phellandrene	α-terpinene	β-phellandrene	γ-terpinene	p-mentha-3,8-diene	terpinolene	isoterpinolene	p-cymene	polymers
α-Terpinene	0,02	–	—	92.8	—	3,5	—	—	—	—	3,7
	0,08	—	—	74.8	<0.1	20.9	—		<0,1	<0.1	4,3
	0,17	<0,1	<0.1	70.2	<0,1	23,4	—	—	0.8	1,4	4.2
	5	0,1	<0.1	68.3	0,1	23.2	<0,1	<0.1	2.3	1.5	4,7
	10	0 5	<0,1	59,9	1 4	19,4	0,9	0.1	3,2	2,0	12.7
	20	0 4	<0,1	36 5	1,1	13.7	2 4	0,1	20.9	2,2	22,7
	30	0,5	0 1	33,9	0,1	12,6	2,3	0,1	25,7	2,4	22.4
	60	0,4	0,2	33.9	0,1	12,3	2,2	0,2	25,8	2,2	22,8
γ-Terpinene	0,02	—	—	6.3	—	92,5	—	—	—	1,1	0,1
	0,08	<0,1	<0.1	8,2	—	89,4	—	—	—	1,4	1.0
	0,17	0,1	<0.1	49.9	—	47,3	—	—	<0,1	1.5	1.3
	1	0,4	0,1	62,3	<0,1	28,8	<0.1	—	5,7	1,9	0,9
	5	0.4	0,3	45.9	1.2	17,2	2,9	<0,1	29.2	1,8	1,1
	10	0,5	0.5	47.0	0,1	16,4	3,3	0,1	29,2	2,0	1.0
	20	0,6	0,4	45 8	0.1	15,6	3,2	0,2	31,3	2,1	0,8
	30	0,5	0 5	45,6	0,1	15 4	3,4	0,2	31,6	1,8	1,0
Terpinolene*	0,17	—	—	5,7	—	0,1	0,1	64,0	26.3	–	0,6
	1	<0.1	<0.1	22.0	—	7,5	5,6	3,3	54.8	0.7	2,8
	10	0,5	0,4	36,5	<0,1	12,4	3.4	0,7	34.9	0,6	7.3
	20	0,2	0,2	40,5	0.1	13.1	2 5	0,7	28.1	1 6	9,7
	30	0 3	0 4	40,7	0,2	12,6	2,6	0.5	27,0	1,5	9,6
(+)-trans-Isolimonene	0.02	—	—	—	—	—	4,8	0,1	95.2	—	
	0.17	—	—	<0 1	—	—	6 6	2,7	90,7	—	—
	1	—	—	2,3	—	0,2	7,6	2,9	73.9	<0,1	13,1
	10	—	—	14.3	—	4,6	5,3	1.9	56,4	1 9	15.6
	30	0,5	0,4	23 8	0,1	11,7	2,7	0,6	22.1	10,8	17.3
(+)-Limonene†	0,02	—	-	10,5	-	<0 1	—	—	89.5	—	—
	0,08	—	—	23,1	—	7,7	—	—	69.2	—	—
	0.17	<0,1	—	31 6	<0,1	17 4	<0,1	—	39,6	4.8	6.3
	0,5	0.9	<0.1	47,2	1.6	10,7	4.1	—	21.6	7.9	5.9
	6	1,8	0.1	37.0	1,4	11,4	3,7	<0,1	22.5	11,8	10.2
	10	1,2	0.2	36,2	0,2	10.8	2,7	0.2	23,3	12,7	12.5
	20	1.5	0,6	35,3	0,6	11.0	2,3	0 4	23,1	12,2	13,0
	20‡	0.4	0,2	25.9	0,2	9.3	2.1	0.2	18,1	21,2	22.4

---

*The reaction products contained 3.3-4.6% of an unknown component.

†At 150°C, the degrees of conversion (%) after the given times (h) were, respectively: 0.5 after 0.02, 1.5 after 0.08, 12.5 after 0.17; 44 after 0.5; 51 after 6, 52 after 10; 52.5 after 20; and 97 after 20.

‡At concentrations of $KOC(CH_3)_3$ and limonene in dimethyl sulfoxide of 0.90 and 0.63 M, respectively.

γ-Terpinene in converted first into α-terpinene, cymene, and polymers. The amount of the terpinene (I) rises and reaches a maximum of 62% after 1 h. Appreciable amounts of the menthadienes (IX) and (XI) are formed after 5 min, of isoterpinolene after 10 min, of the menthadienes (VIII) and (X) after 1 h, and of terpinolene after 5 h. After 20 h, a mixture is formed which scarcely changes further with time and has the same quantitative composition as in the case of the terpinene (I). As compared with the mixture obtained from terpinene (I), however, this mixture contains a twenty times smaller amount of polymers and a correspondingly larger amount of menthadienes. After the reaction has been proceeding for 10 min, 36% of the terpinolene has been converted into a mixture of the menthadienes (I) and (VII) (ratio 1:4.5) containing traces of the menthadienes (II) and (VIII). In the course of time, the amount of the menthadienes (I) and (VII) in the reaction mixture rises, the amount of (VII) becoming a maximum (55%) after 1 h and that of (I) a maximum (40%) after 20 h. The menthadienes (IX) and (XI) and (X) are formed in appreciable amounts after 1 and 10 h, respectively when the amount of the terpinenes (I) and (II) in the reaction mixture has risen considerably. A mixture of menthadienes, cymene, polymers, and an unknown component, which does not change its composition further, is formed after 20 h.

After only 1 min, (+)-trans-isolimonene is converted completely into a mixture containing the menthadienes (VII) and (VIII) (ratio 20:1) and traces of terpinolene. In the course of time, the amounts of the menthadienes (III) and (VIII) rise, and after 1 h they have reached maxima — 2.9 and 7.6%, respectively — and the amount of isoterpinolene has fallen. Appreciable amounts of the terpinene (I) appear in the reaction products 10 min from the beginning of the reaction, and of the terpinene (II) after 1 h, when the amount of the terpinene (I) is 2%. Subsequently, the amounts of the menthadienes (III) and (VIII) decrease and those of the terpinenes (I) and (II) rise and small amounts of the menthadienes (IX), (X), and (XI) appear in the mixture. After 30 h a mixture of reaction products is formed which is similar in its qualitative composition to the mixtures formed from the terpinenes (I) and (II).

In contrast to the menthadienes (I-IV), the transformation of limonene under the action of potassium tert-butanolate in dimethyl sulfoxide was studied at 150°C, since at 50°C the hydrocarbon underwent no change during 1 h, and at 100°C the degree of its transformation was only 12%. At 150°C the degree of transformation of limonene after 10 h reached 52% and did not change further. Only with an increase in the concentration of potassium tert-butanolate in dimethyl sulfoxide from 0.25 to 0.9 M did the degree of transformation of limonene rise to 97%. At the same time, the amounts of cymene and polymers increased by a factor of 1.7.

Limonene is converted first into a mixture containing the menthadienes (I) and (VII) (ratio 1:8.5) and traces of the terpinene (II). In the course of time, the amount of terpinene rises and reaches a maximum: for (I) after 0.5 h (47%), and for (II) after 10 min (17%). The amount of isoterpinolene falls. Appreciable amounts of the menthadienes (VIII), (X), and (XI) are formed after 10 min and of the menthadienes (IX) and (III) after 0.5 and 6 h, respectively. After 6 h a mixture of reaction products similar in qualitative composition to the mixtures formed from the menthadienes (I), (II), and (IV) is produced. After 10 h, a mixture of reaction products is formed which does not change further under these conditions with an increase in the time of the reaction.

Simultaneously with the isomerization, dehydrogenation, and polymerization reactions of limonene, its racemization takes place, as has been observed previously under the action of N-lithioethylenediamine [1]. This is shown by the change in the optical purity of the limonene that we used in the reaction and those isolated from the products of the reaction that had proceeded for 10 and 60 min (93, 75 and 45%, respectively).

The mixtures of the products of isomerization, dehydrogenation, and polymerization reactions of the menthadienes studied (I-V) that change no further with an increase in the time of the reaction are not the thermodynamic equilibrium mixtures since their quantitative composition depends on the nature of the initial menthadiene, and, as can be seen for the case of limonene as an example, on the amount of catalyst. According to the literature [1, 2], at the thermodynamic equilibrium only the products of the isomerization reaction are present. In these circumstances, the main primary product of the isomerization of the terpinene (I) is the terpinene (II), of the terpinene (II) the terpinene (I), of the

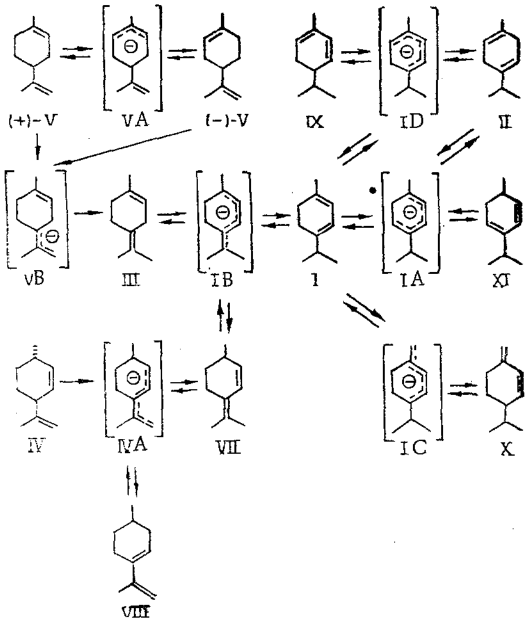

TABLE 2. Properties of the Hydrocarbons

Hydrocarbon No.	Purity, %	$[\alpha]_D^{20}$, deg	d_4^{20}	n_D^{20}	Hydrocarbon No.	Purity, %	$[\alpha]_D^{20}$, deg	d_4^{20}	n_D^{20}
I*	100	0	0,8352	1,4780	IV‡	—	+213	0,8296	1,4650
I†	99	0	0,8378	1,4779	V*	100	+118	0,8482	1,4721
I‡	—	—	0,8341	1,4783	V†	98	+95	0,8414	1,4727
II*	100	0	0,8503	1,4746	V†	98	+57	0,8458	1,4731
II†	97	0	0,8518	1,4762	V‡	—	+126	0,8411	1,4743
II‡	—	—	0,8498	1,4735	VI†	99	0	0,8589	1,4908
III*	100	0	0,86 6	1,4911	VI‡	—	—	0,8573	1,4904
III‡	—	—	0,8596	1,4896	VII†	100	0	0,8565	1,5062
IV*	100	+202	0,8279	1,4538	VII‡	—	—	0,8561	1,5059

*Initial hydrocarbon.

†Reaction product.

‡According to the literature: (I-III, V, VI) [8], (IV) [7], (VII) [9].

menthadienes (III) and (V) the menthadienes (I) and (VII), and of isolimonene (IV) the menthadienes (VII) and (VIII).

Supplementing the scheme of the transformations of limonene given in the literature [1] by the results obtained in the present investigation, the isomerization transformations of the p-menthadienes can be represented in the form of a general scheme according to which their transformations proceed through the corresponding pentadienyl carbanions (IA-D, IVA, VA) of activated menthadiene—potassium tert-butanolate—dimethyl sulfoxide complexes with the formation first of the corresponding primary isomerization products and then of an equilibrium mixture of the menthadienes (I-III), (VII-XI). According to the scheme given by Ferro and Naves [1], cymene is formed as the result of the detachment by the base of a proton from a carbanion (IA or ID). The formation of polymers probably takes place by an anionic polymerization mechanism [4] with the addition of the carbanions to the double bonds of the menthadienes.

EXPERIMENTAL

The IR spectra of the hydrocarbons (I-V, VI, VII) were taken in a thin layer on a UR-20 instrument. GLC analysis was carried out on two liquid phases: a mixture of 1,2,3-tris-β-cyanoethoxypropane and diethyleneglycol adipate (column A) and squalane [5]. The relative retention times on column A were: XI) 0.52, IV) 0.64, IX) 0.88, I) 1.00, V) 1.07, X) 1.25, II) 1.45, VIII) 1.62, III) 1.81, VII) 1.95, VI) 2.15; unknown component — 2.42.

Preparative GLC (PGLC) was performed on a PAKhV-04 instrument at 110°C using a composite column filled with Chromaton N-AW-DMCS (0.25-0.316 mm fraction) impregnated with poly(ethylene adipate) (20%, length 6 m) and 1,2,3-tris-β-cyanoethoxypropane (15%, length 9 m). The carrier gas was nitrogen.

Fractional distillation was performed in a column with an efficiency of 120 theoretical plates.

The initial menthadienes (I-V) (Table 2) were obtained in the following way: the terpinenes (I) and (II) by the fractional distillation of the product of the isomerization of dipentene with p-toluenesulfonic acid [6], with the purification of the enriched fractions by the PGLC method; the menthadienes (III) and (V) by the fractional distillation of pine oleoresin turpentine and of fennel oil, respectively; and isolimonene from the product of the thermal isomerization of 2-carene [7].

The transformation of the p-menthadienes (I-V) was carried out in sealed ampules with heating of the freshly redistilled menthadienes with a solution $KOC(CH_3)_3$ in dry dimethyl sulfoxide (DMSO): the menthadienes (I-IV) at 50°C with concentrations of $KOC(CH_3)_3$ and menthadiene in DMSO of 0.25 and 0.90 M, respectively; and limonene at 150°C with concentrations of $KOC(CH_3)_3$ and limonene in DMSO of 0.25 and 0.90 M and of 0.90 and 0.63 M, respectively. The reaction product was diluted with water and extracted with ether. The extract was washed with saturated aqueous NaCl, and dried with $MgSO_4$, and the ether was distilled off through a reflux condenser first at atmospheric pressure and a bath temperature of 40-50°C and then at a residual pressure of 15 mm Hg and a bath temperature of 20°C. The hydrocarbon fraction with residual ether was analyzed by the GLC method using pentane as internal standard. Then the reaction product was weighed with an accuracy of ±0.0002 g, the volatile fraction was distilled off completely, the residue was weighed, and the amount of polymers was calculated with allowance for the amount of ether in the sample and a correction for the wetting of the walls of the flask with volatile fraction. The composition of the reaction products was calculated from the results of two parallel determinations on the basis of the results of GLC analysis and the weight of the polymers. The results are given in Table 1.

The reaction products obtained from the menthadienes (I-V) were identified from the RRTs of the hydrocarbons and by the method of adding authentically pure substances in the performance of GLC.

The hydrocarbons (I, II, VI, and VII) (Table 2) were isolated from the products of the reaction of the terpinene (I), performed for 20 h, by fractional distillation followed by the purification of the enriched fractions by PGLC. From the products of the reaction of limonene performed for 10 and 60 min the PGLC method permitted the isolation of limonene (Table 2).

The IR spectra of the hydrocarbons isolated (I, II, V, VI, and VII) were identical with those given in the literature [10].

SUMMARY

The products of the transformation of α- and γ-terpinenes, terpinolene, (+)-trans-isolimonene, and (+)-limonene under the action of potassium tert-butanolate in dimethyl sulfoxide contain — in addition to the α- and γ-terpinenes, isoterpinolene, p-mentha-3,8-diene, and p-cymene found previously — terpinolene, α- and β-phellandrenes, p-mentha-2,4-diene (in a total amount of 1-3%), and polymers. Under these conditions, limonene is racemized. The primary products of the isomerization reaction have been identified. A supplementary scheme of the isomerization transformations of the p-menthadienes is presented.

LITERATURE CITED

1. A. Ferro and Y.-R. Naves, Helv. Chim. Acta, 57, 1141 (1974).
2. S. Bank, C. A. Rowe, A. Schriesheim, and L. A. Naslund, J. Org. Chem., 33, 221 (1968).
3. A. B. Booth, US Patent No. 3,407,242 (1968); Chem. Abstr. 70, 47638 (1969).
4. J. E. Germain, Catalytic Conversion of Hydrocarbons, Academic Press, New York (1969).
5. I. I. Bardyshev, L. A. Popova, and É. F. Buinova, Vestsi Akad. Nauk BSSR, Ser. Khim., No. 4, 112 (1976).
6. T. Farmer, British Patent, No. 1,130,975 (1968); Chem. Abstr., 70, 58060 (1969).
7. I. I. Bardyshev, Zh. F. Loiko, A. L. Pertsovskii, and L. A. Popova, Dokl. Akad. Nauk SSSR, 194, 325 (1970).
8. Short Chemical Encyclopaedia [in Russian], Moscow, Vol. 2 (1963), p. 967; Vol. 5 (1967), pp. 112, 113, 859.
9. H. Pines and H. E. Eschinazi, J. Am. Chem. Soc., 77, 6314 (1955).
10. B. M. Mitzner, E. T. Theimer, and E. K. Freeman, Appl. Spectrosc., 19, 169 (1965).