The filling of the polyethylene film with the substance can also be effected in the vapor phase (Fig. 3b) also with the use of minimum amounts of the compounds under investigation.

The design features of the execution of an experiment and the procedure of filling the substances permit the use of the film method for recording both highly volatile and strongly hydrolyzed compounds. As examples, Fig. 4 presents the IR absorption spectra of $Cl_3SiCH_2GeCl_3$, an easily hydrolyzed compound, which were recorded in a cuvette with KBr windows and according to the film method. Figure 4 presents the portion of the spectrum containing the bands of the Ge—C, Ge—Cl, and Si—Cl stretching vibrations.

The experimental features of the film method considered above make it possible to evaluate its effectiveness in the investigation of the absorption spectra of chemical compounds and provide some aid for choosing a particular recording method in each specific case.

We thank I. V. Obreimov for taking an interest in the work.

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APPLICATION OF ^{1}H NMR AND ^{13}C NMR FOR ESTABLISHING THE SPATIAL STRUCTURE OF STEREOISOMERIC o- AND p-MENTHANE, o- AND p-MENTHENES, AND ISOPROPYLCYCLOHEXANE

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The spatial orientation of substituents in stereoisomeric o- and p-menthenes has a significant influence on their reactivity [1]. The purpose of the present work was to establish the spatial structure of stereoisomeric o- and p-menthanes, 8-o- and 8-p-menthenes, and isopropylcyclohexane on the basis of an analysis of the ^{1}H NMR and ^{13}C NMR spectra. The parameters of the spectra of the compounds which we synthesized are presented in Tables 1 and 2. In the following we shall present evidence of the structure of the substances obtained on the basis of an analysis of the spectra.

Isopropylcyclohexane (I)

It is known [2] that the chemical shift of the carbon atoms in unsubstituted cyclohexane is $\delta_C = 27.50$ ppm and that a C^1 axial methyl group causes an upfield shift of the resonance of C^3 and C^5 due to 1,3-syn—axial coupling. An equatorial CH_3 group has practically no effect on the chemical shift of C^3, C^4, and C^5. Therefore, with consideration of the Overhauser effect and the results of experiments with incomplete suppression of the proton—carbon spin—spin coupling, the line at $\delta_C = 20.10$ ppm may be assigned to the two CH_3 groups in the isopropyl fragment, and the line at $\delta_C = 27.38$ ppm may be assigned to C^3, C^4, and C^5. The line located at the lowest field, $\delta_C = 44.86$ ppm, should be assigned to C^1. The line at $\delta_C = 33.55$ ppm also has the lowest peak intensity, and we assigned it to C^7. In fact, if we carry out a calculation of the chemical shift according to the scheme in [3, 4], the expected value is equal to $\delta_C = 33.03$ ppm, which demonstrates the validity of the assignment.

Thus, according to Barton's rule, the ^{13}C NMR spectrum points out the realization of a predominant chair conformation with an equatorial orientation of the isopropyl group. The features just described with consideration of the laws in methylcyclohexane [5] are reflected in Table 3.

cis-o-Menthane (II) and trans-o-Menthane (III)

The assigned chemical shifts are summarized in Table 1. From the data in Table 3 it is seen that the chemical shifts of C^2 in the *a*e and ee isomers differ sharply, the shift being

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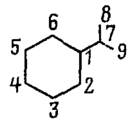
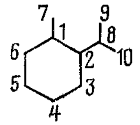
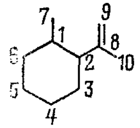
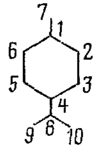
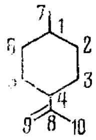
TABLE 1. Carbon-13 Chemical Shifts of Isopropylcyclohexane and Stereoisomeric o- and p-Menthanes and 8-o- and 8-p-Menthenes

Compound	Formula	Configuration	Chemical shift, ppm									
			C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}
I		e	44,86	30,69	27,38	27,38	27,38	30,63	33,55	20,10	20,10	—
II		ae	34,99 31,8	48,24 50,0	25,07 25,2	27,94 27,3	22,75 22,0	30,06 32,6	11,93	30,81	20,88	20,88
III		ee	36,93 36,2	50,32 53,7	25,17 30,6	27,32 27,1	27,32 27,4	36,93 36,3	15,81	35,11	20,31	21,66
VIII		ae	34,36	48,06	25,39	27,39	23,09	30,82	13,14	149,02	109,07	21,54
IX		ee	36,15	54,60	33,29	27,32	27,32	35,31	19,32	149,22	110,96	20,88
IV		ae	29,66 28,6 29,54	32,00 32,6 31,72	25,95 25,2 25,70	43,48 44,7 43,45	25,95 25,2 25,70	32,00 32,6 31,72	19,58 19,99	30,86 30,72	20,56 20,42	20,56 20,42
V		ee	33,49 33,0 35,95	36,22 36,3 33,23	30,44 30,6 30,13	44,47 44,5 44,22	30,44 30,6 30,13	36,22 36,3 33,23	23,09 22,87	33,49 35,95	20,23 19,41	20,23 19,41
VI		ae	28,76	32,07	26,87	44,55	26,87	32,07	18,94	150,29	108,76	21,41
VII		ee	32,73	35,64	32,07	45,35	32,07	35,64	22,06	148,38	108,04	20,82

Note. The values underlined by a continuous line were calculated with the use of the increments in Table 3; the values underlined by a dashed line were obtained in [6].

TABLE 2. Parameters of the ^1H NMR Spectra of Stereoisomeric o- and p-Menthanes and o-Menthenes

Compound	Configuration	Chemical shift, ppm			$^3J_{HCH_3}$, Hz
		CH_3	C^8H	$C(CH_3)_2$	
cis-o-Menthane	*ae*	—	—	0,82 d	
				0;89 d	7,0
		0,87 d	—	—	6,5
trans-o-Menthane	*ee*	—	2,04 m	0,74 d	
			—	0,89 d	7,0
		0,85 d	—	—	5,7
cis-p-Menthane	*ae*	—	1,63 m	0,87 d	6,65
		0,92	—	—	6,5
trans-p-Menthane	*ee*	—	—	0,87 d	6,65
		0,88 d	—	—	5,5
cis-8-o-Menthane	*ae*	0,79 d	—	1,68* s; 4,65 m	
				and 4,82 m†	7,0
trans-8-o-Menthane	*ee*	0,79 d	—	1,56 s *	
				4,12 d †	6,0; 1,2 ‡

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*Chemical shift of the methyl group in $CH_3-C=C$

†Chemical shift of the terminal methylene group $C=CH_2$.

‡$^4J_{HH'}$.

displaced to higher fields in the *ae* isomer. The equatorial isopropyl group shifts the C^2 resonance 17.3 ppm to a lower field, and the C^1 axial methyl group shifts the resonance 5.2 ppm in the same direction. The equatorial methyl group shifts the resonance to a lower field to an even greater extent (+8.9 ppm). Therefore, the C^2 resonance in the *ae* isomer should occur at a higher field than the resonance of the same carbon atom in the ee isomer, as is observed experimentally.

The assigned configuration is also confirmed by the chemical shift of the C^1 methyl group. According to [5], in derivatives of 1,1-dimethylcyclohexane, whose molecules exist in a predominant chair conformation, the resonance of the carbon atom of the axial methyl group occurs at a higher field than does that of the analogous carbon atom in the equatorial position. The *ae* and ee isomers under discussion, in fact, display a similar law (δ_C = 11.93 ppm for the *ae* isomer and δ_C = 15.81 ppm for the ee isomer).

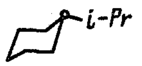
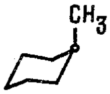
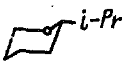
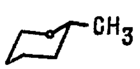
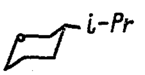
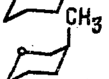
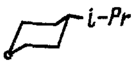
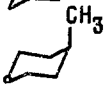
Our attention is attracted to the isochronism of the gem-dimethyl fragment in the *ae* isomer and the anisochronism (δ_C = 20.30 ppm and 21.66 ppm) in the ee isomer. This anisochronism is clearly a consequence of the chirality of C^2 in the two isomers. In addition, attention should be focused on the C^5 chemical shift. In the *ae* isomer the resonance of this carbon atom is shifted to higher fields. This finding may be understood on the basis of the data in Table 3. In fact, when an axial CH_3 group is present on C^1 and a predominant chair conformation is realized, the line of C^5 should be shifted to higher fields, as is observed experimentally (δ_C = 22.75 ppm for the *ae* isomer and δ_C = 27.32 ppm for the ee isomer).

cis-p-Menthane (IV) and trans-p-Menthane (V)

In cis- and trans-p-menthane the chemical shifts of C^2, C^6, and C^7 may be analytical indicators of the configuration of the compounds. According to Table 3, an equatorial isopropyl group has a small influence (−0.1 ppm) on the chemical shift of the δ-carbon atoms of the cyclohexane ring. However, an equatorial CH_3 group influences this carbon atom in such a manner that its resonance is shifted significantly (+8.9 ppm) to a lower field, while an axial CH_3 group produces a shift in the same direction, but to a lesser extent (+5.2 ppm). Therefore, in the ee isomer the C^2 and C^6 resonances should be at lower fields than the resonances of the analogous atoms in the *ae* isomer, as is observed experimentally. The configurational assignments are also confirmed by the chemical shifts of the carbon atoms of the CH_3 group. In the *ae* isomer the shift has the value δ_C = 19.58 ppm, and in the ee isomer the value is 23.09 ppm.

The results of the experiments with incomplete suppression of the proton–carbon spin–spin coupling do not contradict the assigned chemical shifts, which are in good agreement

TABLE 3. Influence of Methyl and Isopropyl Groups on the ^{13}C Chemical Shifts of Cyclohexane [$\delta(C_6H_{12})$ = 27.5 ppm]*

Compound	Chemical shift	Compound	Chemical shift	Compound	Chemical shift
	$+5,6$ppm .		$+17,3$		$+1,2$
	$+8,9$		$+3,1$		$+5,2$
	0,0		—0,1		—5,4
	—0,3		—0,1		—0,1

Note. A minus sign indicates an upfield shift, and a plus sign indicates a downfield shift.

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*The carbon atom whose chemical shift is under consideration is marked by a circle.

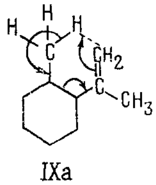
(especially in the case of trans-p-menthane) with the values calculated on the basis of the increments in Table 3 and, at the same time, point out the significant disparity between the values found and the values calculated with the use of the data in [6].

cis-8-p-Menthene (VI), trans-8-p-Menthene (VII), cis-8-o-Menthene (VIII), and trans-8-o-Menthene (IX)

The characteristic feature noted above in the carbon chemical shifts are completely duplicated in the spectra of these compounds, i.e., the classification of the compounds as *ae* or ee isomers is confirmed by the ^{13}C NMR spectra.

We studied the PMR spectra of the stereoisomeric compounds described (Table 2). The protons of an axial CH_3 group usually resonate at higher fields than do those of an equatorial group ($\Delta\delta_{ae}$ = 0.06 ppm); however, this difference is too small to argue configurational assignments with great confidence. A similar tendency is observed in the isomers of the compounds studied. It should be noted that the indicated anisochronism of the gem-dimethyl groups is also manifested in the proton spectra.

The data in the ^{13}C NMR spectra can serve as evidence of intramolecular interactions in the hydrocarbons studied. For this purpose it is convenient to use the difference between the values of the chemical shifts of analogous atoms in stereoisomeric analogs ($\Delta\delta^n_{ee-ae}$). As has previously been noted [1], in order to explain the increased reactivity of cis-8-o-menthene (VIII) and trans-8-p-menthene (VII) in comparison to trans-8-o-menthene (IX) under the conditions of acid–base catalysis, it has been postulated that there is a possibility of the formation of a pseudoring in the last compound under the action of the steric and electronic effects:

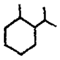
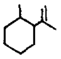
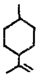


IXa

In structure IXa, C^2 and C^7 have increased electron densities; therefore, their screening is increased, and the chemical shift should be displaced to a lower field. Table 4 shows the influence of the type of substitution and the nature of the substituent on the value of $\Delta\delta^n_{ee-ae}$.

In cis- and trans-8-p-menthene the considerable spatial distance between the substituents eliminates the possibility of intramolecular association. Therefore, the value of $\Delta\delta C_{ee-ae}$ for C^4 located in the α position relative to the isopropenyl group (0.8 ppm) scarcely differs from that calculated for the stereoisomeric p-menthanes (0.99 ppm).

TABLE 4. Influence on the Type of Substitution and the Nature of the Substituent on $\Delta\delta^{n}_{Ce-\alpha e}$

Carbon atom	Compound			
				
C^2	2,08 ppm	6,54	4,22	3,57
C^4	—0,62	—0,07	0,99	0,80
C^7	3,88	6,18	3,51	3,12

The vicinal diequatorial configuration of the substituents in trans-o-menthane, as has already been noted, results in the anisochronism of the gem-dimethyl groups of the isopropyl fragment due to the chirality of the C^2 atom in the α position relative to it and an increase in $\Delta\delta C^{2}_{ee-\alpha e}$ to 2.08 ppm. The replacement of the isopropyl fragment by an isopropenyl fragment results in an increase in this parameter in the case of the stereoisomeric 8-o-menthenes by a factor of 3.1 (6.54 ppm).

The laws indicated are duplicated upon examination of $\Delta\delta C^{7}_{ee-\alpha e}$ for the ortho and para isomers under discussion. More specifically, the stereoisomeric p-menthanes and 8-p-menthenes have similar values (3.51 ppm and 3.12 ppm, respectively), while in the case of the stereoisomeric o-menthanes and 8-o-menthenes the difference reaches a factor of 1.6 (3.88 ppm and 6.18 ppm, respectively).

Thus, the data from the ^{13}C NMR spectra confirm the possibility of the formation of a pseudoring for trans-8-o-menthene by means of intramolecular association.

The ^{13}C NMR spectra were recorded on a Bruker-Phyzik WH-90 spectrometer with a resonance frequency for the observation of the ^{13}C NMR equal to 22.63 MHz under conditions of broadband decoupling from the protons at 36°C. The resonance conditions were stabilized according to the ^{2}H NMR signal. We used 8-50% solutions in benzene. The chemical shifts are given in ppm relative to TMS. The measurements were carried out relative to the signal of the solvent (benzene) with a subsequent recalculation [$\delta(C_6H_6)$ 128.7 ppm relative to TMS].

The ^{1}H NMR spectra were recorded on a Varian HA-100D spectrometer for 10% solutions of the samples in benzene. The internal reference was TMS. The accuracy in the measurement of the values of the chemical shift was ±0.01 ppm, and that of the measurement of the spin–spin coupling constant was ±0.1 Hz.

The separation of the mixtures of stereoisomers (II and III, IV and V, VI and VII) into the individual substances was effected by vacuum rectification in a column with 80 theoretical plates. The gas-chromatographic analysis was carried out under the conditions previously described in [7]. The preparative gas–liquid chromatography of the compounds (I-III, VI, VII) was carried out on a PAKhV-03 chromatograph. A stainless steel column 9 m long with an internal diameter equal to 6 mm was filled with Chezasorb AW-HMDS (0.2-0.36 mm) impregnated with 15% Silicone DS-550. The temperature was 113°C. The flow rate of the argon was 140 ml/min.

I. Cumene (3 g) in hexane (50 ml) was reduced by a calcium hexammine–i-C_3H_7OH system according to the procedure in [8]. The product obtained (the yield was 86% of the cumene taken) was subjected to exhaustive hydrogenation in absolute methanol (8 ml) at 20°C in the presence of Raney nickel (0.5 g). The usual treatment yielded 2.4 g of a product, from which isopropylcyclohexane was isolated, T_b = 153 to 154°C (753 mm Hg), d_4^{20} 0.8036, n_D^{20} 1.4405, MR_D 41.43. Calculated: 41.56.

II and III. During the hydrogenation of o-cymene (86 g) [9] at 200-210°C under a pressure of 80-100 atm in the presence of palladinized charcoal (0.9% Pd relative to the weight of the original o-cymene) over the course of 4 h, 1.88 g-mole of H_2 were absorbed. After removal of the catalyst from the reaction products, stereoisomeric o-menthanes were isolated. Their parameters were, respectively, T_b = 66-67°C (19 mm Hg) and 54-55°C (13 mm Hg), d_4^{20} 0.8231 and 0.8103, n_D^{20} 1.4501 and 1.4458, MR_D 45.78 and 46.13. Calculated: 46.18.

IV and V. These isomers were obtained by the hydrogenation of dipentene (145 g, 95% purity, d_4^{20} 0.8432, n_D^{20} 1.4731) at 75-90°C under a pressure of 35-40 atm in the presence of palladinized charcoal (0.8% Pd relative to the weight of the original dipentene). Over the course of 2 h, 1.83 g-mole of H_2 were absorbed. After the removal of the catalyst from the reaction product, the stereoisomeric p-menthanes were isolated. T_b = 56-57°C (15 mm Hg) and 58-59°C (14 mm Hg), d_4^{20} 0.8086 and 0.7954, n_D^{20} 1.4432 and 1.4378, MR_D 45.98 and 46.25. Calculated: 46.18.

VI and VII. During the hydrogenation of 123 g of α-terpineol* (95% purity, synthetic pine oil, Technical Specifications No. 81-05-66-77) at 20°C under atmospheric pressure in the presence of Raney Ni (11 g) over the course of 82 h, 0.72 g-mole of H_2 was absorbed. The usual treatment yielded 115 g of a product, from which cis-p-menthan-8-ol (X) with T_m = 43-44.5°C, p-nitrobenzoate with T_m = 87-88°C, trans-p-menthan-8-ol (XI) with T_m = 34-35°C, and o-nitrobenzoate with T_m = 97-98°C [11] were isolated by rectification followed by adsorption chromatography on Al_2O_3 [10].

The dehydration of alcohols X and XI with freshly fused $KHSO_4$ [10] yielded cis- and trans-8-p-menthene, T_b = 34-34.5°C (4 mm Hg) and 33-34°C (4 mm Hg), d_4^{20} 0.8282 and 0.8132, n_D^{20} 1.4603 and 1.4531, MR_D 45.73 and 45.95. Calculated: 45.71.

The elemental analysis of compounds I-VII correspondedto the theoretically calculated values.

cis-8-o-Menthene and trans-8-o-menthene were previously synthesized in [12, 13].

We thank P. P. Chernov for measuring the chemical shifts in the ^{13}C NMR spectra.

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*25% solution in $i-C_3H_7OH$.